Hanna Vehkamäki

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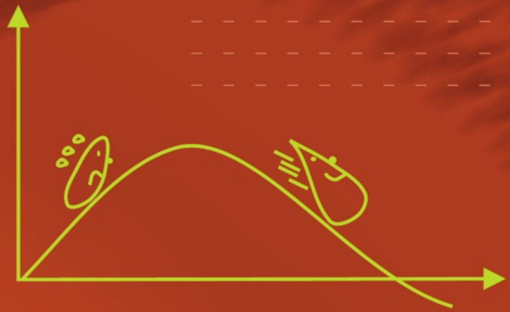

Springer

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With 62 Figures and 7 Tables

Springer

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DOI 10.1007/b138396
ISBN-10 3-540-29213-6 Springer Berlin Heidelberg New York
ISBN-13 978-3-540-29213-5 Springer Berlin Heidelberg New York
e-ISBN 3-540-31218-8

Library of Congress Control Number: 2005934783

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Typesetting: By the Author
Production: LE-TEX, Jelonek, Schmidt & Vöckler GbR, Leipzig
Coverdesign: design&production, Heidelberg

Printed on acid-free paper 2/YL – 5 4 3 2 1 0

To Seraphina

Preface

This book is based on my course in classical nucleation theory given at the Department of Physical Sciences, University of Helsinki, Finland. I want to thank Ari Asmi for producing the first electronic version of my lecture notes, and all my colleagues and students who have commented on the manuscript of this book, especially Kaisa Hautio, Lauri Laakso, Antti J. Lauri, Anni Määttänen and Ismo Napari. I am grateful to professor Markku Kulmala for support during preparation of this book and the Academy of Finland for funding. I thank Adam Foster for checking the language of the manuscript.

Helsinki, August 31st 2005 *Hanna Vehkamäki*

Contents

List of symbols

Variables (Latin alphabet):

symbol	*explanation*	*unit*
A	surface area	m^2
$\mathcal{A}$	activity	1
A_1, A_2	areas between curves in (P, v) diagrams	J
a	van der Waals constant	Nm^4
$\mathcal{B}$	magnetic flux density	T
b	van der Waals constant	m^3
b	interaction parameter in the Ising model	1
C	concentration of clusters	$1/\mathrm{m}^3$
C_P	heat capacity at constant pressure	J/K
C_V	heat capacity at constant volume	J/K
C_n	number of conditions	1
d	auxiliary variable in heterogenous nucleation	m
d_X	auxiliary variable in heterogenous nucleation	1
$\bar{e}_\lambda$	eigenvector	$\mathrm{s}^{1/2}$
F	Helmholtz free energy	J
F^e	normalization factor of cluster size distribution	$1/\mathrm{m}^3$
f	auxiliary notation for $\Delta\varphi/(kT)$	1
f_φ, f_V	geometric factors in heterogenous nucleation	1
G	Gibbs free energy	J
g_v	Gibbs free energy per volume unit	J/m^3
H	enthalpy	J
h	enthalpy per molecule	J
h	height, depth	m
I, $\bar{I}$	flow, flow vector of clusters	$1/(\mathrm{s\ m}^3)$
I_1, I_2, I_3, I_4	areas under curves in (P, v) diagrams	J
i	index, or number of molecules, of component 1	
J	nucleation rate	$1/(\mathrm{m}^3 s)$
j	index, or number of molecules, of component 2	

Variables (Latin alphabet):

symbol	*explanation*	*unit*
K_T	isothermal compressibility	1/Pa
k, k'	index of phase	
L	length	m
$\mathcal{M} = \cos\vartheta$	cosine of the contact angle	1
m	mass of a cluster/molecule	kg
N	number of molecules	1
$\mathcal{N}$	maximum cluster size in the system	1
$\{N_{i,l}\}$	molecular composition of a multicomponent cluster	1
$\{N_{i,l}, N_{k,l}\}$	molecular composition of a multicomponent cluster with component k highlighted	1
n	number of components	1
n	number of molecules in the cluster	1
$\underline{O}$	orthogonal matrix	
P	pressure	Pa
P_x	auxiliary pressure	Pa
$P'_{i,x}$	auxiliary pressure	Pa
p	number of phases	1
R	radial coordinate in the droplet	m
$\underline{R}$	growth matrix	1/s
R_p	radius of the pre-existing particle	m
r	radius of droplet	m
RH	relative humidity	
S	saturation ratio	1
$\mathcal{S}$	entropy	J/K
s	enthalpy per molecule	J/K
s_l	z-component of the spin	1
T	temperature	K
t	time	s
t_r, t_{Rp}	tangents of surfaces	
U	internal energy	J
V	volume of the system/phase	m^3
V_n	number of variables	1
v	molecular volume, partial molecular volume	m^3
$\mathcal{W}$	number of microstates	1
$-W^*$, $\underline{W}^*$	second derivative of the formation free energy for critical cluster or matrix of them	J
W_{11},W_{12},W_{22}	second derivatives of the formation free energy for critical cluster	J
$X = R_p/r$	ratio of preexiting particle radius to cluster radius	1
x	mole fraction	1
x, y	auxiliary coordinates/variables	
Z	Zeldovich factor	1

Variables (Greek alphabet):

symbol	*explanation*	*unit*
β	condensation coefficient	1/s
Γ	activity coefficient	1
$\underline{\Gamma}$	matrix product $\underline{\Gamma} = \underline{R}^{*1/2} \underline{W}^{*} \underline{R}^{*1/2}$	J/s
γ	evaporation coefficient	1/s
δ_i	mean diffusion jump distance	m
$\Delta e_{i,\mathrm{des}}$	desorption/adsortion energy per molecule	J
$\Delta e_{i,\mathrm{diff}}$	activation energy for diffusion per molecule	J
ΔH^e	phase transition enthalpy, latent heat	J
Δh^e	phase transition enthalpy, latent heat per molecule	J
ΔN^*	number of molecules in the cluster compared to the cluster volume filled with gas	1
$\overline{\Delta n}$	vector representing cluster size compared to the critical size	1
$\overline{\Delta \eta}$	vector representing cluster size in modified variables	$\mathrm{s}^{1/2}$
ΔQ	change of heat	J
$\Delta U^*_{l,p}$	energy of the cluster compared to the same molecules in pure bulk liquids	J
ΔV^e	phase transition volume	m^3
Δv^e	phase transition volume per molecule	m^3
ΔW	work done	J
ε	interaction parameter in Ising model	J
ζ	surface tension parameter in Ising model	1
θ	direction angle of the critical cluster flow vector	radian
ϑ	contact angle	radian
ι_1, ι_2, $\bar{\iota}$	flow of clusters in modified variables	$\mathrm{s}^{-1/2}$
λ	integer multiplier	1
λ	eigenvalue	J/s
μ	chemical potential	J
μ_s	magnetic dipole moment	J/T
$\nu_{i,\mathrm{des}}$	frequency of vibrations lading to desorption	1/s
$\nu_{i,\mathrm{diff}}$	frequency of vibrations lading to diffusion	1/s
ξ	cluster concentration in modified variables	$1/(\mathrm{m}^3\mathrm{s})$
ρ	number density	$1/\mathrm{m}^3$
σ	surface tension	N/m
φ	free energy	J
ϕ	direction of the vector connecting the origin with the critical size	radian
ϕ	auxiliary angle in heterogenous nucleation geometry	radian
ψ	auxiliary angle in heterogenous nucleation geometry	radian
Ω	Grand potential, grand free energy	J

Sub- and superscripts:

$_0$	constant, bath property, initial state
$_{1\ 2\ 3}$	component
$_c$	critical point
$_{\mathrm{cap}}$	related to cap in heterogenous nucleation
$_{\mathrm{coex}}$	phase equilibrium, coexistence
$_e$ ^{e}	equilibrium, saturation
$_{\mathrm{eq}}$	equilibrium
^{eS}	supersaturated equilibrium
$_d$	total of droplet: bulk liquid +surface
$_g$	gas, vapour
$_{\mathrm{het}}$, $^{\mathrm{het}}$	heterogeneous nucleation
$_{\mathrm{hom}}$, $^{\mathrm{hom}}$	homogeneous nucleation
$_i$	component i
$_j$	component j
$_l$	liquid
$_{\mathrm{max}}$	maximum
^{p}	pure compound
$_s$	surface
$_{\mathrm{sol}}$	solid phase
$_{\mathrm{surf}}$	surface term
^{T}	transpose
^{t}	transition point
$_{\mathrm{tot}}$	total of different phases/subsystems/components/clusters
$^{\mathrm{vapour}}$	related to vapour
$_{\mathrm{vol}}$	volume term
$_x$	related to average/virtual monomer
$_{x,y}$	related to auxiliary coordinates x,y
* $_*$	critical cluster
$'$	auxiliary system

Constants:

k Boltzmann constant	$1.3806503 \cdot 10^{-23}$J/K
g gravitation acceleration	9.81 m/s^2
π	3.14159265

Operators:

d	derivative	
∂	partial derivative	
Δ	change, difference	
$đ$	inexact differential	
	infinitesimal change which is not a differential of any function of state	
$đQ$	infinitesimal change of heat	J
$đW$	infinitesimal work done	J
∇	gradient, vector differential operator	

Foreword

When a thermodynamic system is about to undergo a first order phase transition, nucleation is the appearance of the first tiny nuclei of the new phase in a metastable mother phase. Microscopic bubbles appear in a liquid that starts to boil, and droplets are formed in a condensing vapour. The solidification of melted metal in a foundry, the transition from quark-gluon plasma to hadron matter about 10 milliseconds after the Big Bang, and the freezing of cryopreservatives as well as strawberries are all phase transitions initiated by nucleation. Nucleation is a common and basic physical phenomenon, the details of which are still poorly understood.

Nucleation phenomena have been studied for almost 300 years (Zettlemoyer 1977). Understanding of the metastable states started to emerge when Fahrenheit (1724) found out that the freezing point of water is not unique, but depends on the freezing conditions. For example, boiled, air-free water in sealed vessels was still liquid after being kept several hours at -9 °C. The addition of ice to supercooled water initialised ice formation. During the eighteenth and nineteenth centuries, other workers extended these observations to other substances and systems. Lowitz (1795) and Gay-Lussac (1813) investigated supersaturation phenomena in aqueous salt solutions, and pointed out the analogy with supercooled water. Gay-Lussac (1819) and Berthelot (1850, 1860) discovered that the supersaturation of gases dissolved in water, the superheating of a liquid above its boiling point, and the formation of bubbles in over-expanded liquids are phenomena analogous to supercooling. It was noticed that mechanical operations such as shaking could cause the supersaturated solutions to crystallise, and that certain seed particles, like the crystals of the new phase, caused crystallisation, while some other seed particles were ineffective. Water in small capillary tubes or as small drops in an immiscible liquid was found to remain in the liquid state far below 0°C. De Coppet (1875) measured the time lags before crystallisation occurred in solutions having a known supersaturation. Ostwald (1879) divided supersaturated solutions into two classes, metastable and labile. In the absence of seed nuclei, metastable solutions are unchanged for unlimited time periods, while labile ones crystallise spontaneously in a short period of time. For the same solute in the same solvent, an increase in concentration turns a metastable solution to a labile one. Metastable and labile regions were observed also in supercooled melts. In 1880 Aitken (Aitken 1881, 1897) observed that dust and salt particles act as condensation nuclei for water vapour in the atmosphere. Von Helmholtz (1886, 1887, 1890) investigated the formation of mist in a water vapour jet. If water vapour is led through a nozzle into air, it cools down and becomes supersaturated. Normally, the jet is hardly visible, but in the presence of, for example, dust or acid fumes the jet becomes densely white or coloured.

Laplace (1806) laid a foundation for the classical theory of nucleation by deriving the condition for the mechanical equilibrium of a surface separating two phases. W. Thomson (later lord Kelvin) (1870, 1871) used the result of Laplace and derived the Kelvin (Gibbs-Thomson) equation, which shows that the saturation vapour pressure over a curved surface of a liquid is greater than the saturation vapour pressure over a flat surface of the same liquid. J.J. Thomson (1888) modified W. Thomson's result and showed that the melting point of a small crystal is lower than that of a larger one. Ostwald (1900) adapted the Kelvin equation to show that the solubility of a crystal decreases when the size of the crystal grows. The Kelvin equation led to qualitative understanding of supersaturation and supercooling phenomena. The origin of these phenomena was understood, but the process leading to the phase change was still obscure. The first step toward understanding the kinetics of phase change were taken by Gibbs (1906), who suggested that the stability of the existing phase can be measured by finding out the work needed to form a nucleus of the new phase within it. When a nucleus of sufficient size is formed, it tends to grow further until the supersaturation is relieved. Volmer and Weber (1925) recognised that the metastability is related to the kinetics of the transition. They realised that the probability of formation of nuclei is closely related to the formation energy of the nuclei. Szilard and Farkas (Farkas 1927) described the kinetic mechanism of supersaturated vapours, and during the thirties and the forties several workers investigated the kinetics of phase transitions. The classical theory of nucleation was derived by Becker and Döring (1935), and Zeldovich (1942, 1943). It is based on an approximative, analytical solution of kinetic equations describing growth and decay of nuclei in the metastable state.

Many of the pioneers of nucleation studies are responsible for remarkable achievements that have made them widely famous:

- John Aitken (1839–1919), a Scottish physicist and meteorologist, built his own apparatus, a koniscope, to study microscopic particles in the atmosphere, and concluded that they are vital to the formation of droplets in clouds and fogs. Atmospheric particles belonging to a certain size range are still called Aitken mode particles (Gittings and Munro 2005).

- French chemist Pierre Eugène Marcelin Berthelot (1827–1907) studied, among other topics, thermochemistry, organic syntheses and the history of alchemy. In 1868 he analysed samples of the Orgueil meteorite and reported finding in them hydrocarbons comparable with the oils of petroleum (EuCheMS 2000).
- German physicist Gabriel Daniel Fahrenheit (1686–1736) lived mostly in England and Holland making meteorological instruments and, especially, constantly improving thermometers. He is most famous from the thermometric scale known by his name and still extensively used in the United States (Encyclopædia Britannica 2005).
- French chemist Joseph Luis Gay-Lussac (1778–1850) studied properties of gases. In 1808 he came to the conclusion that pressure of a certain amount of gas is proportional to its temperature. This finding, preceding the full equation of state of an ideal gas is know as Gay-Lussac's law. He also took part in the discovery of the element boron (Bowden and Michalovic 2000).
- American physicist Josiah Willard Gibbs (1839–1903), was the first to write down the differential form of the first law of thermodynamics. He derived a large variety of consequences from this equation spanning the fields of elasticity, surface phenomena, phase transitions and chemistry. He also wrote a classic book "Elementary Principles in Statistical Mechanics" (Weart 1976).
- German physicist Hermann Ludwig Ferdinand von Helmholtz (1821–1894) studied mechanics, heat, light, electricity and magnetism, and concluded that all them are manifestations of energy, which he called force. He formulated a theory which stated that electric and magnetic forces propagate instantaneously at distance. He also tried to show that oxidation of foodstuff was behind the muscular action of animals (O'Connor and Robertson 2001).
- Pierre-Simon Laplace (1749–1827), a French physicist and mathematician, was active in many fields, which is testified by the various equations carrying his name. He transformed Newton's mechanics from geometrical notation to calculus, and proved that the solar system is stable. He was possibly the first user of the phrase "it is easy to see" in derivations, and as usual, could not himself fill the gaps afterwards without days of works. He studied probability, the speed of sound, was first to calculate the value of integral $\int_{-\infty}^{\infty} e^{-x^2}\,dx = \sqrt{\pi}$. He determined specific heats for many substances using a calorimeter of his own design, invented gravitational potential ψ and showed that it satisfies Laplace's equation $\nabla^2\psi = 0$. He worked on unified theory of mechanical, thermal and optical phenomena. Laplace's integral transform is one tool for solving ordinary differential equations. Laplace was for a while a minister of the interior during Napoleon's reign (Weisstein 2005).
- Wilhelm Ostwald (1853–1932) was born in Riga, but lived later in Germany. He studied electrochemistry and chemical dynamics, and discovered a law of dilution named after him. In 1909 Ostwald was awarded the No-

bel Prize for Chemistry for his work on catalysis, chemical equilibria and reaction velocities (Nobel Foundation 2005b).

- Leo Szilard (1898–1964) was Hungarian born, but later American physicist, who took part in the studies of nuclear fission. During the second world war he worked in the Manhattan project toward the nuclear bomb. After the war he took part in designing nuclear reactors, then started campaigning for world peace and moved to the field of biology (Simkin 1997).
- Joseph John Thomson (1856–1940) was an English physicist, who studied cathode rays. He determined that the rays consist of small negatively charged particles, which, he realised, must be part of all matter. He thus discovered the first subatomic particle, the electron, and suggested the plum-pudding model for the atom. In 1906 he was awarded the Nobel Prize in physics for his research into the discharge of electricity in gases (Nobel Foundation 2005a).
- William Thomson (1824–1907), also known as lord Kelvin, was a Scottish physicist. He studied thermodynamics, and proposed the absolute temperature scale scientists most often use. He also observed what is now called the Joule-Thomson effect, namely the decrease in temperature of a gas when it expands in a vacuum. He calculated the age of the Earth based on its cooling rate assuming that it was originally part of the Sun. He became rich and was created Baron Kelvin of Largs in 1866 due to his participation in a telegraph cable project after his mirror-galvanometer was used in the first successful sustained telegraph transmissions in a transatlantic submarine cable (O'Connor and Robertson 2003).
- Max Volmer (1885–1965) was a German physicist, who studied electrochemisty and gave his name to the Butler-Volmer equation describing reactions controlled by electrochemical charge transfer process. After the second world war he was forced to work in the Soviet Union in the area of atomic physics 1945–1955, after which he returned to (East) Germany (Katz 2003).
- Yakov Borisovich Zeldovich (1914–1987) was a Soviet physicist. He studied the oxidation of nitrogen in explosions and other explosion related phenomena like shock-waves and flame propagation. He also took part in the study of fission in the decay of uranium. Later he took an interest in quark annihilation and neutrino detection in cosmology. In 1967 he proposed that the universe was originally homogeneous and isotropic, but expansion has led to non-isotropy (Tenn 2003).

1

Fundamentals of thermodynamics

In this chapter we briefly list all the thermodynamic concepts needed in classical nucleation theory. The readers should make sure that they are familiar with this fundamental thermodynamic machinery and, if needed, refer to textbooks of thermodynamics to fully understand the basics before heading forward to phase equilibrium and nucleation theory. This chapter also serves to introduce the notation used in this book.

1.1 Phases

Different phases have the same molecules or mixtures in them, but they are ordered differently. Different *order* means that

- Mobility of molecules with respect to their neighbours differs
- Correlations of molecular locations and orientations differ

If we know the position and orientation of one certain molecule, how much does that tell us about the neighbouring molecules?

Gas – not a lot
Liquid – somewhat more ↓ Order increases
Solid state – almost everything

We will use the words *gas* and *vapour* interchangeably. To be really strict, vapour is a gas that can condense, so it depends on temperature whether some gas can be called a vapour as well. Water is clearly a vapour at room temperature, but argon only at very low temperatures. *Fluid* is a common word for liquid and gas.

The order parameter measures the order.

- In gas-liquid-solid transition: the order parameter is density of molecules $\rho = n = \frac{N}{V}$ [1/ m^3] or volume per molecule $v = \frac{1}{\rho} = \frac{V}{N}$ [m^3]
- In magnetic systems the order parameter is magnetisation, see Fig. 1.1

- In a binary alloy the order is the pattern of molecules in the lattice, see Fig. 1.2.

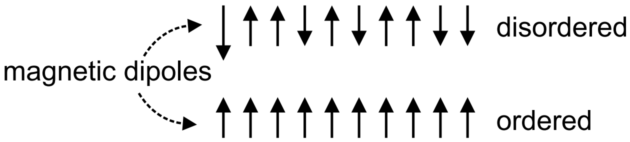


Fig. 1.1. Order in magnetic systems.

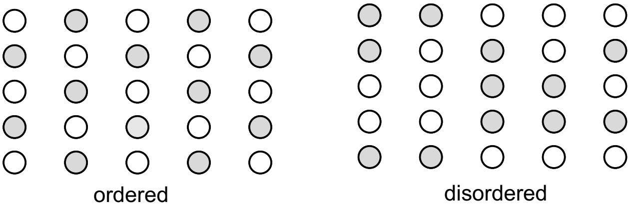


Fig. 1.2. Order in binary alloys.

1.2 System, state and state variables

A *system* is defined as the area we focus on. It is separated from the rest of the universe, *environment*, by a real or an imagined wall. Examples:

-  Inside a rigid container, the volume and number of molecules constant,
-  Inside an imagined box, the volume constant, number of molecules change.
-  A certain set of molecules, the number of molecules constant, volume changes, imagined wall moves so that it encompasses selected molecules.
- Flexible container (“balloon”) – volume changes, number of molecules constant.

The system interacts with the environment in various ways. The system can be

- *Isolated*: no interaction which means no work is done by the system to the environment or by the environment to the system, and there is no heat or particle exchange.
- *Insulated*: no heat exchange.

- *Closed*: no particle exchange.
- *Open*: both energy (work and heat) and particles can come and go.

State is short for *equilibrium state*, where nothing changes in the macroscopic properties of the system, nothing moves macroscopically (microscopic thermal motion always exists above 0K temperature), no heat or particles flow. State is defined by a set of measurable quantities, *variables of state*, for example volume (V), pressure (P), temperature (T) and number of molecules (N_i). All the other quantities describing the system can be calculated when the variables are measured. The calculated properties are uniquely defined for each state and they are called *functions of state*. For example:

$$\left.\begin{array}{ll} U & \text{energy}\\ \mathcal{S} & \text{entropy}\\ \rho=\frac{N}{V} & \text{density}\\ \mu & \text{chemical potential}\end{array}\right\}\text{these can not normally be measured directly}$$

All the measured quantities are not necessarily independent. *Equation of state* gives the dependences, For example: $V = V(P, T, N)$ or $P = P(T, V, N)$ or $T = T(P, V, N)$ or $N = N(T, P, V)$. One variable can be chosen to be a function of state. We measure the ones that are easy to measure and calculate the rest. So the division between variables and functions of state is arbitrary – we can choose. Variables and functions are divided into extensive and intensive quantities as shown in Table 1.1

Table 1.1. Intensive and extensive quantities.

Extensive:	put two similar systems together and the quantity in the joint system is double the original
	$\boxed{N}+\boxed{N}=\boxed{2N}$
	$\boxed{V}+\boxed{V}=\boxed{2V}$
	$\boxed{U}+\boxed{U}=\boxed{2U}$
	$\boxed{\mathcal{S}}+\boxed{\mathcal{S}}=\boxed{2\mathcal{S}}$
Intensive:	the quantity does not change when doubling the system size
	$\boxed{T}+\boxed{T}=\boxed{T}$
	$\boxed{P}+\boxed{P}=\boxed{P}$
	$\boxed{\rho}+\boxed{\rho}=\boxed{\rho}$
	$\boxed{\mu}+\boxed{\mu}=\boxed{\mu}$

NOTE: Heat and work are not quantities (variables or functions) of state: there is no point in asking how much heat/work is in a system with certain T, P *and* N. *Only changes of heat* ΔQ *or work* ΔW *in a process are reasonable concepts. So do not ever write* Q *or* W, *only* ΔQ, ΔW, $\text{đ}Q$ *and* $\text{đ}W$. *"đ" tells that change of heat/work between two states* $A(P_A,T_A,N_A)$ *and* $B(P_B,T_B,N_B)$ *depends also on what kind of process took the system from A to B.*

1.3 What is chemical potential?

The definition of chemical potential of component i is (see also p. 11)

$$\mu_i = \left(\frac{\partial U}{\partial N_i}\right)_{\mathcal{S},N_{i\neq j},V,A} .$$

The chemical potential μ_i is the change in system energy when entropy, number of particles of components $j \neq i$, surface area and volume are kept constant, and one molecule of component i is added to the system. So it is the sum of kinetic and interaction energies of one molecule in a certain system. The chemical potential depends on system temperature (how much kinetic energy a molecule has), pressure (how close a molecule is forced to other molecules), and composition (what kind of molecules our molecule i interacts with). It is difficult to imagine how we could arrange a experimental set-up where entropy is constant. Thus a more practical definition of chemical potential can be given in terms of free energies which will be introduced in section 3.1.

The most commonly used definition is in terms of the Gibbs free energy G (p. 46)

$$\mu_i = \left(\frac{\partial G}{\partial N_i}\right)_{T,P,N_{i\neq j}} . \tag{1.1}$$

As soon as we understand what is Gibbs free energy, it is easy to imagine how to use this definition: keep the temperature and system pressure constant, add in one molecule of component i and measure the Gibbs free energy change. Another definition is

$$\mu_i = \left(\frac{\partial F}{\partial N_i}\right)_{T,V,N_{i\neq j}} ,$$

where F is the Helmholtz free energy (see p. 46).

1.4 What is entropy?

Entropy $\mathcal{S}$ describes the macroscopically hidden microscopic possibilities of variation in the system. Let us think we can measure only the total energy U of a system, but we know we have 5 particles and 3 possible microscopic energy levels for each particle with energies 0 J, 1 J and 2 J (see Fig. 1.3):

- If the macroscopic state is $U = 10$ J we have to have all particles on the 2 J level, 10 J $= 5 \times 2$ J, thus there is only one possibility.
- If the macroscopic state is $U = 5$ J we can have:
  2×2 J + 1×1 J + 2×0 J
  1×2 J + 3×1 J + 1×0 J = 3 possibilities
  5×1 J
- Try $U =$ 9,8,7,6,4,3,2,1 J yourself.

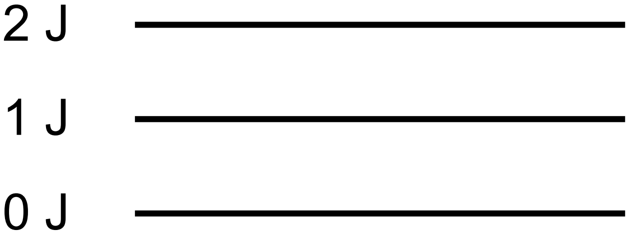


Fig. 1.3. Diagram of energy levels.

The entropy is defined as

$$\mathcal{S} = k \ln \mathcal{W}, \tag{1.2}$$

where $\mathcal{W}$ is the number of hidden microscopic combinations and k is the Boltzmann constant $1.38 \cdot 10^{-38}$ J/K. The unit of entropy is that of the Boltzmann constant $[\mathcal{S}] = \mathrm{J/K}$. For the example illustrated in Fig. 1.3 we have
$U = 10\ \mathrm{J} \rightarrow \mathcal{S} = k \cdot \ln 1 = 0$
$U = 5\ \mathrm{J} \ \rightarrow \mathcal{S} = k \cdot \ln 3 > 0.$

What is the number of possibilities for a gas with volume V and particle number N to have energy U? Positions and velocities of all molecules can be arbitrary, only V, N and U are restricted. Is the number infinite? The answer is no, because of quantum mechanics: a particle in a box can only have certain velocities and the place can be determined only to an accuracy given by the Heisenberg uncertainty principle. Thus entropy is not infinite either.

NOTE 1:

$$\begin{cases} \textit{Temperature } T & \textit{is proportional to the total kinetic energy of particles} \\ \textit{Energy } U & \textit{is the total kinetic + interaction energy of particles} \end{cases}$$

kinetic energy can transform to potential energy and back, but the total energy is conserved in an isolated system.

NOTE 2: Division between what is macroscopic and what is microscopic depends on the measurement tools/level of modelling or thinking: how small details we can and want to measure and calculate.

1.5 Laws of thermodynamics

The thermodynamic theory is build on four cornerstones called the laws of thermodynamics which are listed here.

Zeroth law : “Temperature and thermometer exist.”

First law : “Conservation of energy.”

$$dU = \text{đ}Q - \text{đ}W + \sum_i \mu_i dN_i. \tag{1.3}$$

See Fig. 1.4 for the sign conventions of the quantities in eq. (1.3) listed in

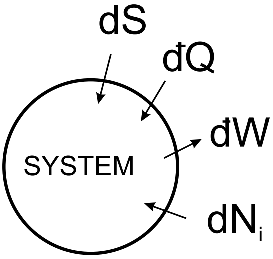


Fig. 1.4. Sign conventions of flows.

Table 1.2

Table 1.2. Quantities needed to formulate the first law of thermodynamics.

dU	Change in internal energy of system (function of state)
$\text{đ}Q$	Tiny amount of heat that has flown into the system. $\text{đ}Q < 0$ if heat flows out of the system
$\text{đ}W$	Tiny amount of work performed by the system. $\text{đ}W < 0$ if work is performed by the surroundings
μ_i	Chemical potential for species i in the system
dN_i	Number of molecules of type i that have moved into the system.
N_i	the number of molecules in the system.

In this book we handle systems with many components $i = 1,2,\ldots,n$. For example in a three component system
N_1 is number of water molecules
N_2 is number of sulphuric acid molecules
N_3 is number of ammonia molecules

Second law: "For an isolated system, all possible processes occur so that total entropy increases in time."

$$\frac{dS}{dt} \geq 0. \tag{1.4}$$

Spontaneous processes are the ones that happen in an isolated system without any involvement of the environment. In equilibrium no spontaneous processes are possible: this implies that it is not possible to increase $\mathcal{S}$ by microscopically reorganising the system while the macroscopic state stays unchanged. Entropy has its maximum possible value at given conditions, $\mathcal{S} = \mathcal{S}_{\max}$.

$$\boxed{\text{Equilibrium in an isolated system} \Leftrightarrow \mathcal{S} \text{ has its maximum value}}$$

Third law: “When we approach 0 K entropy goes to zero.”

1.6 Reversible processes, volume work and surface work

Reversible process: a process that can also occur in a reversed direction. In the reversed process all the changes that occurred in the system and also in the *environment* must be undone. For a reversible process in an isolated system:

$$\begin{aligned} d\mathcal{S} &\geq 0 \text{ Process possible} \\ -d\mathcal{S} &\geq 0 \text{ Reverse process is also possible} \end{aligned}$$

The only solution to satisfy both of these conditions is to have $d\mathcal{S} = 0$.

$$\boxed{\text{Process reversible} + \text{system isolated guarantees that } \mathcal{S} \text{ is constant}}$$

A reversible process has to be very slow, *quasi-static*, and always infinitely close to an equilibrium state. For a reversible process heat flow into the system $đQ = Td\mathcal{S}$. While $đQ$ is often problematic to define or calculate, as it depends on how the process is conducted, $Td\mathcal{S}$ is the change in the function of state, and thus unambiguous.

Volume work: Work done when the volume V of the system is changed by dV (reversibly)

$$đW_V = PdV$$

$dV > 0$ V increases, system “pushes out” – performs work to the environment. Work done by the system $đW_V = PdV > 0$ and energy change of the system $dU = -đW_V < 0$, which is logical since system loses energy when it expands.

Surface work: Work done when the area A separating two phases is changed by dA (reversibly)

$$đW_A = -\sigma dA$$

σ is surface tension, and its units are $[\sigma] = \frac{[E]}{[A]} = \frac{\mathrm{J}}{\mathrm{m}^2} = \frac{\mathrm{Nm}}{\mathrm{m}^2} = \frac{\mathrm{N}}{\mathrm{m}}$. The thermodynamic definition (see p. 11) of surface tension is

$$\sigma = \left(\frac{\partial U}{\partial A}\right)_{\mathcal{S},N_i,V} .$$

Surface tension is the energy change of the system when entropy, number of particles and volume are kept constant, but the surface area in the system is increased. Thermodynamic surface tension has natural units $\mathrm{J/m^2}$, energy per unit area. This energy arises due to the fact that molecules on the surface of, for example, some liquid feel less attraction from their neighbours than the molecules in the interior of the bulk liquid. Attraction is weaker because surface molecules are not fully surrounded by other liquid molecules. Weaker attraction means less negative energy, so the energy of the system rises because of surface formation.

Mechanically, surface tension is the magnitude F of the force exerted parallel to the surface of a liquid divided by the length L of the line over which the force acts, see Fig. 1.5. Surface tension acts to make the surface area as small as possible. The natural unit for mechanical surface tension is N/m, force per length unit. The values of thermodynamic and mechanical surface tension should be equal if the former is defined at the surface of tension, see p. 57.

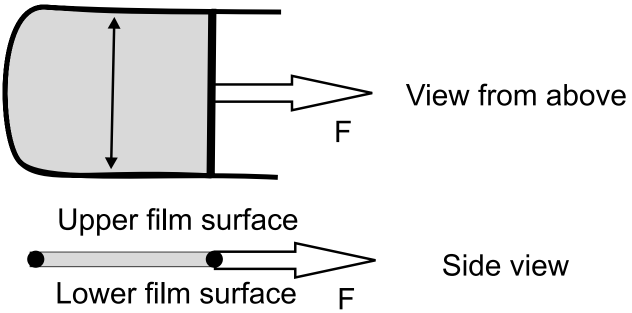


Fig. 1.5. Apparatus, consisting of a U-shaped wire frame and a wire slider, that can be used to measure the surface tension of a liquid (Wiley InterScience 1999-2005).

A practical way of obtaining the value of gas-liquid (or gas-solid) surface tension from molecular interactions, for example in computer simulations, is to first calculate the energy of a cubic sample of a liquid, which is in the middle of a larger liquid container. Then the cube is divided into two parts, which are taken far away from each other, both still surrounded by liquid from all other sides but one (see Fig. 1.6). The area of the "cut" surface is A and the energy difference between the unified and split liquid cubes is ΔE, and the surface tension is $\sigma = \Delta E/(2A)$.

Surface tension is normally positive $\sigma > 0$, and so is the surface area $A > 0$, thus when we increase the surface area, surface work is negative $đW_A = -\sigma dA < 0$ and the energy change of the system is positive $dU =$

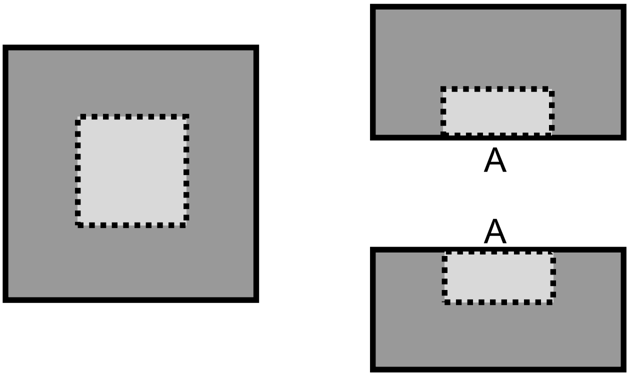
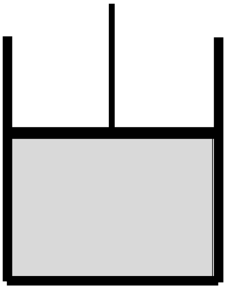


Fig. 1.6. Liquid cube as a whole (left) cut into two halves which are taken far from each other (right). The free surface of the sample cube after the split is two times A. The cube is immersed in a large container of the same liquid.

$-đW_A = \sigma dA$. Again this is logical since increasing the surface area puts more energy to the system (Think of a balloon: we have to do work to increase the surface area. In thought experiments a balloon skin is often a good analogy to use for surface tension).

NOTE: There can be other kinds of work as well, like stirring (typically not reversible).

1.7 Why is volume work not always $P\Delta V$?



It may sound strange that $đW = PdV$ only for a reversible process. Think of a container filled with gas: When the lid is allowed to move, why is the work not PdV?

Because the thermodynamic pressure $P = -\left(\frac{\partial U}{\partial V}\right)$ is not equal to the average force F per area of the lid $P_F = \frac{F}{A}$, which is mechanical pressure on the lid. The mechanical pressure and density of molecules is different in different places in the container. The molecules do not move instantly to the extra space when the lid moves. If the system is heated, temperature rises on one side of the system first and then the heat transports to the rest of the system: temperature is not the same everywhere, and the process is irreversible. When the heating is very slow, the process is almost reversible.

$$\boxed{\text{For an irreversible process : } \text{đ}Q < Td\mathcal{S},\ \text{đ}W < PdV}$$

$dU = \text{đ}Q - \text{đ}W + \sum \mu_i N_i$ is still the same for both irreversible and reversible processes if the initial and final states are the same. It has to be, since U is a function of state and dU depends only on final and initial states, not on the process.

Reversible processes never happen in real life, but we can use them to calculate changes in functions of state between initial and final equilibrium states!

1.8 Fundamental equation

We know an expression for the differential of energy, dU, but how does energy itself, $U = U(\mathcal{S}, V, N_i, A)$, look like as a function? This is the question we aim to answer. We start with the first law for a reversible case

$$\boxed{dU = Td\mathcal{S} - PdV + \sum_i \mu_i dN_i + \sigma dA. \qquad (1.5)}$$

The derivation of the fundamental equation is based on realising which of the variables and functions of state in the first law are intensive and which are extensive:

$$\begin{array}{c} \text{INTENSIVE} \\ dU = \overset{\Downarrow}{T}\ \underset{\Uparrow}{d\mathcal{S}} - \overset{\Downarrow}{P}\ \underset{\Uparrow}{dV} + \sum_i \ \overset{\Downarrow}{\mu_i}\ \underset{\Uparrow}{dN_i} + \overset{\Downarrow}{\sigma}\ \underset{\Uparrow}{dA} \\ \text{EXTENSIVE} \end{array}$$

The extensive variables $\mathcal{S}$, V, N and A can be chosen as variables of state. U, T, P, μ and σ depend on them as functions of state.[1] Let us put λ similar systems together. Energy and all other extensive variables scale with λ:

$$\lambda U = U(\lambda \mathcal{S}, \lambda V, \lambda N_i, \lambda A).$$

We take the derivative of this equation with respect to λ:

$$\begin{aligned} U = &\mathcal{S} \left(\frac{\partial U}{\partial(\lambda \mathcal{S})} \right)_{\lambda V, \lambda N_i, \lambda A} + V \left(\frac{\partial U}{\partial(\lambda V)} \right)_{\lambda \mathcal{S}, \lambda N_i, \lambda A} \\ &+ N_i \left(\sum_i \frac{\partial U}{\partial(\lambda N_i)} \right)_{\lambda V, \lambda N_{j \neq i}, \lambda \mathcal{S}, \lambda A} + A \left(\frac{\partial U}{\partial(\lambda A)} \right)_{\lambda V, \lambda N_i, \lambda \mathcal{S}} \end{aligned}$$

---

[1] *NOTE: Entropy is not easy to measure, but let us choose it for a moment as a state variable*

and then set $\lambda = 1$:

$$\begin{aligned} U =& \mathcal{S}\left(\frac{\partial U}{\partial \mathcal{S}}\right)_{V,N_i,A} + V\left(\frac{\partial U}{\partial V}\right)_{\mathcal{S},N_i,A} \\ &+ N_i\left(\sum_i \frac{\partial U}{\partial N_i}\right)_{V,N_{j\neq i},\mathcal{S},A} + A\left(\frac{\partial U}{\partial A}\right)_{V,N_i,\mathcal{S}} . \end{aligned} \tag{1.6}$$

We can calculate $\left(\frac{\partial U}{\partial \mathcal{S}}\right)_{V,N_i,A}$ from the first law: set $dV = dN_i = dA = 0$ (V, N_i and A constants):

$$dU\bigg|_{V,N_i,A} = Td\mathcal{S}\bigg|_{V,N_i,A} \Rightarrow \left(\frac{\partial U}{\partial \mathcal{S}}\right)_{V,N_i,A} = T.$$

Similarly we can calculate derivatives of energy with respect to volume, particle numbers and area of the system

$$\left(\frac{\partial U}{\partial V}\right)_{\mathcal{S},N_i,A} = -P, \text{ note here the sign!}$$

$$\left(\frac{\partial U}{\partial N_i}\right)_{\mathcal{S},N_{j\neq i},V,A} = \mu_i$$

and

$$\left(\frac{\partial U}{\partial A}\right)_{\mathcal{S},N_i,V} = \sigma.$$

These are the actual thermodynamic definitions of T, P, μ_i and σ. We substitute T, P, μ_i and σ in the place of derivatives in eq. (1.6) and we get the *fundamental equation*

$$\boxed{U = T\mathcal{S} - PV + \sum \mu_i N_i + \sigma A. \qquad (1.7)}$$

Intensive variables tell us how much does the energy of the system change, if everything else is kept constant but one of the extensive variables changes as shown by Table 1.3.

Table 1.3. Relation of intensive quantities to energy changes in processes where various extensive variables are kept constant.

Constants	Changing parameter	Energy change
V, N_i, A	$\mathcal{S}$	T
$\mathcal{S}$, N_i, A	V	$-P$
V, $N_{j\neq i}$, A, $\mathcal{S}$	N_i	μ_i
V, N_i,$\mathcal{S}$	A	σ

1.9 Gibbs-Duhem and Gibbs adsorption equation

We now derive consistency relations for the changes in intensive quantities. For systems without surface energy, the consistency relation is called the Gibbs-Duhem equation and for systems with surface energy, but no volume energy, the relation is called the Gibbs adsorption equation.

Take the fundamental equation (1.7) for a system with no surface energy term

$$U = T\mathcal{S} - PV + \sum \mu_i N_i$$

and form its total differential

$$dU = Td\mathcal{S} + \mathcal{S}dT - PdV - VdP + \sum d\mu_i N_i + \sum \mu_i dN_i. \tag{1.8}$$

We compare result (1.8) to the reversible version of the first law of thermodynamics (1.5)

$$dU = Td\mathcal{S} - PdV + \sum \mu_i dN_i$$

and notice that the following *Gibbs-Duhem equation* must always be satisfied:

$$\boxed{\mathcal{S}dT - VdP + \sum N_i d\mu_i = 0.} \tag{1.9}$$

In an isothermal case this means

$$\sum N_i d\mu_i = VdP. \tag{1.10}$$

For a system with surface energy, but no volume energy, the fundamental equation has the form

$$U = T\mathcal{S} + \sum \mu_i N_i + A\sigma$$

and its total differential is

$$dU = Td\mathcal{S} + \mathcal{S}dT + \sum d\mu_i N_i + \sum \mu_i dN_i + dA\sigma + Ad\sigma.$$

Again this is compared with the 1st law (eq. 1.5) :

$$dU = Td\mathcal{S} + \sum \mu_i dN_i + \sigma dA$$

which leads to the *Gibbs adsorption equation*

$$\boxed{\mathcal{S}dT + Ad\sigma + \sum N_i d\mu_i = 0.} \tag{1.11}$$

For an isothermal processes this reduces to the *Gibbs adsorption isotherm*

$$\sum N_i d\mu_i + Ad\sigma = 0. \tag{1.12}$$

The Gibbs-Duhem and the Gibbs adsorption equation reflect the fact that thermodynamic relations require different variables/functions of state to be connected in a certain way. As an example we can think along the following lines: Definitions of pressure, volume, number of molecules and temperature feel intuitively clear to us. Entropy is defined through its connection to statistical mechanics (number of microstates). We may have measured or otherwise arrived at an expression for what we think is chemical potential, but if the changes of this "chemical potential" do not follow the Gibbs-Duhem equation when pressure and temperature are changed, we can not call it a "chemical potential" in a thermodynamic sense. Similar arguments can be used in the case of surface tension. For spherical droplets, the value of surface tension depends on the choice of the so-called dividing surface, but only one choice, surface of tension, is consistent with standard thermodynamics, as will be seen on p. 57.

The connection between different variables can be put to use: the Gibbs-Duhem equation with constant temperature and pressure for the two-component case reads

$$d\mu_1 N_1 + d\mu_2 N2 = 0.$$

If we manage to measure the chemical potential for component 1 μ_1 as a function of N_1 and N_2, this equation can be used to calculate the thermodynamically consistent μ_2, and there is no need to measure it. If we can measure both chemical potentials, this equation provides means to check the quality of our measurements.

Problems

1.1. We have five indistinguishable particles and three energy levels 0 J, 1 J, and 2 J. Calculate the entropy for cases where the total energy is 0, 1, 2, 3, 4, 5, 6, 7, 8, 9 and 10 J. Plot the entropy as a function of energy.

1.2. A pot under the Earth's gravity field ($g = 9.81$ m/s^2) contains gas and has a moving frictionless lid (which does not let gas out even when moving). There are three masses m on the lid.
a) We remove first one mass and then another one. How much work does the gas do altogether?
b) We remove two masses simultaneously. How much work does the gas do now?
Note that the processes in a) and b) are irreversible. Do not calculate the work using the equation of state or other thermodynamic information about the gas, because you cannot do so in a process passing through non-equilibrium states.
c) What is the way of removing $2m$ that would give maximum work?
d) What would be the total volume change and work done for an ideal gas and isothermal process where PV=constant. (Initial state is that with three masses and in the final state there is one mass on the lid.)

e) What would be the total volume change and work done for an ideal gas and adiabatic process (no heat exchange with environment, PV$^\gamma$=constant, where γ is the adiabatic constant.)

1.3. Let us have a system obeying virial 3 of state $P = kT\frac{1}{V}\left(1+\frac{B}{V}\right)$ with chemical potential given by $\mu = kT\left(A + \ln\frac{1}{V} + 2\frac{B}{V}\right)$, where A and B are constants. Compare the partial derivatives

$$\left(\frac{\partial\mu}{\partial T}\right)_{V,N}$$

and

$$\left(\frac{\partial\mu}{\partial T}\right)_{P,N}.$$

2

Phase equilibrium

Before studying the process of phase transitions and nucleation, we need to understand phase equilibrium in detail. In this chapter we show how the requirement for maximum entropy can be used to derive phase equilibrium conditions for cases where the two phases are separated by a flat or spherical surface. We also define saturation ratio and activities which describe how far from equilibrium a liquid-vapour system is, and derive a practical form for spherical liquid-vapour equilibrium conditions. As a practical example, we study phase equilibrium in van der Waals fluid.

2.1 Phase equilibrium for a flat surface

First we look at an insulated rigid (= isolated) box, with two phases l and g separated by a flat surface (constant area A, $dA = 0$). The system consists actually of three parts: phase l, phase g and the surface s. Subscripts l, g and s refer to quantities associated with different phases. The energy of phase $l(g)$ is $U_{l(g)}$, entropy is $\mathcal{S}_{l(g)}$ and the number of molecules in that phase is $N_{i,l(g)}$. The volume of the phase is $V_{l(g)}$. The surface also has some energy U_s and entropy $\mathcal{S}_s$, and some molecules $N_{i,s}$ can be on the surface, not in either of the phases l or g. The surface has no volume, only area A. We study reversible processes where the surface moves. The energy change of the surface in such a process is

$$dU_s = T_s d\mathcal{S}_s + \sigma dA + \sum_i \mu_{i,s} dN_{i,s}.$$

The energy chance of phase g is

$$dU_g = T_g d\mathcal{S}_g - P_g dV_g + \sum_i \mu_{i,g} dN_{i,g}$$

and the energy change for phase l is

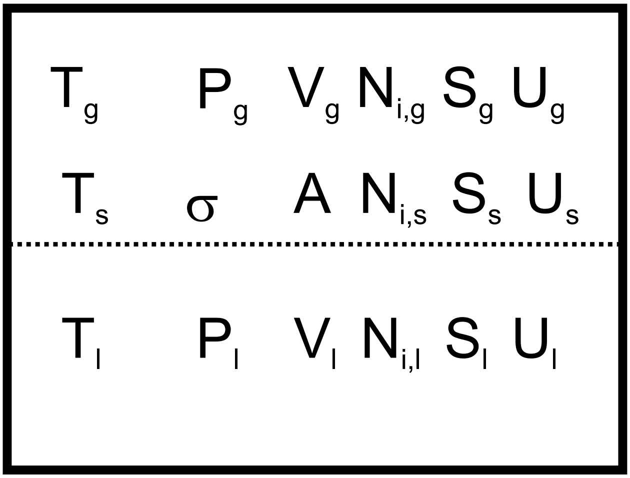


Fig. 2.1. Two phases l and g separated by a flat surface in an insulated and rigid container.

$$dU_l = T_l d\mathcal{S}_l - P_l dV_l + \sum_i \mu_{i,l} dN_{i,l}.$$

We can solve the entropy changes from these three equations and get

$$d\mathcal{S}_s = \frac{1}{T_s}\big(dU_s - \sigma dA - \sum_i \mu_{i,s} dN_{i,s}\big)$$

$$d\mathcal{S}_g = \frac{1}{T_g}\big(dU_g + P_g dV_g - \sum_i \mu_{i,g} dN_{i,g}\big)$$

$$d\mathcal{S}_l = \frac{1}{T_l}\big(dU_l + P_l dV_l - \sum_i \mu_{i,l} dN_{i,l}\big).$$

We get the total entropy of the isolated system by adding up the three entropy contributions

$$d\mathcal{S}_{\text{tot}} = d\mathcal{S}_s + d\mathcal{S}_g + d\mathcal{S}_l.$$

We look for equilibrium, so in an isolated system the total entropy must have a maximum $\mathcal{S}_{\text{tot}} = \mathcal{S}_{\text{tot,max}}$ and for reversible processes $d\mathcal{S}_{\text{tot}} = 0$.

NOTE: Why not $d\mathcal{S}_s = d\mathcal{S}_g = d\mathcal{S}_l = 0$ as well? Because phases g, l and surface are not isolated from each other. They exchange energy and particles, but the whole system is isolated ($d\mathcal{S}_{\text{tot}} = 0$). The insulated and rigid box does not allow energy to escape.

When we search for the maximum entropy we have to keep in mind the following constraints:

1. Energy is constant
$$dU_{\text{tot}} = dU_s + dU_g + dU_l = 0 \Rightarrow dU_s = -(dU_g + dU_l).$$
2. The total volume of the box is constant
$$dV_{\text{tot}} = dV_g + dV_l = 0 \Rightarrow dV_l = -dV_g.$$
3. The total molecular numbers are constant
$$dN_{i,\text{tot}} = dN_{i,s} + dN_{i,g} + dN_{i,l} = 0 \Rightarrow dN_{i,s} = -(dN_{i,g} + dN_{i,l}).$$
4. The area of the flat surface does not change when it moves without changing its shape
$$dA = 0.$$

Now we put all these constraints into the expression for total entropy and arrive at

$$\begin{aligned} d\mathcal{S}_{\text{tot}} = &\left(\frac{1}{T_g} - \frac{1}{T_s}\right) dU_g + \left(\frac{1}{T_l} - \frac{1}{T_s}\right) dU_l + \left(\frac{P_g}{T_g} - \frac{P_l}{T_l}\right) dV_g \\ &+ \sum_i \left(\frac{\mu_{i,g}}{T_g} - \frac{\mu_{i,s}}{T_s}\right) dN_{i,g} + \sum_i \left(\frac{\mu_{i,l}}{T_l} - \frac{\mu_{i,s}}{T_s}\right) dN_{i,l}. \end{aligned} \tag{2.1}$$

Next we will apply a bit of reasoning very typical in thermodynamics. $d\mathcal{S}_{\text{tot}}$ has to be zero for all directions: If we change only U_g, but keep U_l, V_g, $N_{i,g}$ and $N_{i,l}$ constant, $d\mathcal{S}_{\text{tot}}$ has still to be zero.

$$d\mathcal{S}_{\text{tot}} = \left(\frac{1}{T_g} - \frac{1}{T_s}\right) dU_g,$$
$$dU_g \neq 0 \rightarrow T_g = T_s.$$

Similarly, if we change only U_l we get

$$T_l = T_s (= T_g). \tag{2.2}$$

and by changing only one of the other variables we get

$$\begin{array}{rl} \text{changed} & \text{result} \\ V_g : & \dfrac{P_g}{T_g} = \dfrac{P_l}{T_l} \Rightarrow P_g = P_l \qquad (2.3) \\ N_{i,g} : & \mu_{i,g} = \mu_{i,s} \\ N_{i,l} : & \mu_{i,l} = \mu_{i,s} (= \mu_{i,g}) \qquad (2.4) \end{array}$$

NOTE: "All directions"-reasoning is only possible if variables U_g, U_l, V_g, $N_{i,g}$ and $N_{i,l}$ are independent; one of them can be changed without affecting the others. All the constraints have been used before eq. (2.1). For example set

U_g, U_l, V_g, V_l ,$N_{i,g}$ and $N_{i,l}$ are not independent. We have to get rid of V_g or V_l before applying the trick.

The conclusion is that the chemical potentials, temperature and pressure have to be same in all the phases, also the surface phase. Generally in equilibrium temperature and chemical potentials have to be constant in space and time. Otherwise heat or particles flow. Pressure has to be constant in time, but not in space as we shall soon see.

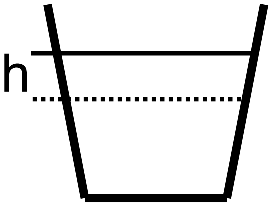


Fig. 2.2. Schematic picture of a glass of water.

NOTE: Many textbooks claim that pressure has to be constant also in space, but this is erroneous. Here is a counter example: Hydrostatic pressure at a depth h in a glass of water (see Fig. 2.2) with density ρ is $P = \rho g h + P_{\text{atmosphere}}$, where g is the gravitation acceleration. This is an equilibrium system. A time-independent force field (gravity) changes the picture for pressure. A column of air in the Earth's atmosphere, however, is not an equilibrium system. Why? There is a temperature gradient and heat flows.

$d\mathcal{S} = 0$ is not enough to guarantee that we have a maximum of $\mathcal{S}$. It could be a minimum or an inflection point without being an extrema at all, or minimum in direction of one variable and maximum in another. For a pure maximum we also have negative second derivative $\frac{\partial^2 \mathcal{S}}{\partial x_i^2} < 0$ for all independent variables x_i. When the following definitions (for a system with no surface phase $A = 0$) are taken into account

$$C_V = \left(\frac{\partial U}{\partial T}\right)_{V,N} = \left(\frac{\text{đ}Q}{\partial T}\right)_{V,N} \text{ heat capacity at constant volume}$$

$$K_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_{T,N} \text{ isothermal compressibility}^{1}$$

the requirements that the second derivatives of entropy are negative lead to the stability conditions

$C_V > 0$	Temperature increase requires heat, does not release it
$K_T > 0$	Pressure increase makes volume smaller
$\left(\frac{\partial \mu_i}{\partial N_i}\right)_{T,V,N_j} > 0$	Chemical potential of a component increases if the number of molecules increase

---

[1] Sometimes in the literature, compressibility is defined with the opposite sign.

NOTE: These stability conditions are only valid for the flat surface case!

If the stability conditions are not valid, every small change from equilibrium moves the system far away from the original state. Common sense tells us that $C_V > 0$ and $K_T > 0$ are very sensible conditions, because added heat increases temperature and added pressure reduces volume. It is also reasonable that pushing one molecule into a certain volume requires more energy the more molecules are already present.

If the system is in an unstable equilibrium, small deviations cause a permanent change. In stable equilibrium entropy has a real maximum and if the system spontaneously or by some external interaction is really moved from the equilibrium, entropy must decrease.

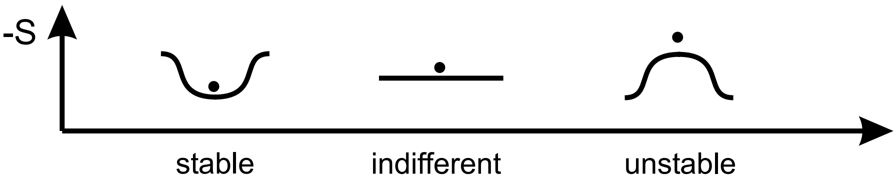


Fig. 2.3. Schematic picture of stable, indifferent and unstable equilibrium states.

2.2 Phase equilibrium for a spherical surface

Now we look at another, more interesting case, where a spherical surface separates the phases. Simple geometric reasoning relates the radius, area and volume of the sphere to each other: radius of the sphere is r and its area is thus $A = 4\pi r^2$. When radius r changes by an infinitesimal amount dr, the change in the surface area is $dA = 8\pi r dr$. The volume of the sphere is $V_l = \frac{4}{3}\pi r^3$, and with the radius change dr it changes by $dV_l = 4\pi r^2 dr$.

We proceed in the same way as when deriving eq. (2.1) for the change of total entropy. The only difference is that now we also have a term $-\frac{\sigma}{T_s} dA$ arising from the energy change of the surface (in section 2.1 surface area change dA was zero, now it is not):

$$\begin{aligned} d\mathcal{S}_{\text{tot}} = &\left(\frac{1}{T_g} - \frac{1}{T_g}\right) dU_g + \left(\frac{1}{T_l} - \frac{1}{T_s}\right) dU_l \\ &+ \left(\frac{P_g}{T_g} - \frac{P_l}{T_l}\right) dV_g + \sum_i \left(\frac{\mu_{i,g}}{T_g} - \frac{\mu_{i,s}}{T_s}\right) dN_{i,g} \\ &+ \sum_i \left(\frac{\mu_{i,l}}{T_l} - \frac{\mu_{i,s}}{T_s}\right) dN_{i,l} - \frac{\sigma}{T_s} dA \\ = &\ 0 \text{ for equilibrium.} \end{aligned} \tag{2.5}$$

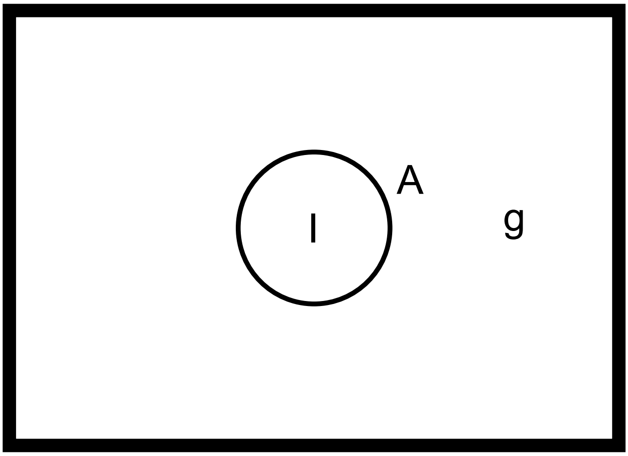


Fig. 2.4. Two phases l and g separated by a spherical surface with area A in an insulated and rigid container.

It is important to notice that we have not used all the constraints yet, and V_g and A are still coupled: total volume stays constant which means $dV_g + dV_l = 0$, and leads to $dV_g = -dV_l = 4\pi r^2 dr$ and the area change $dA = 8\pi r dr$ can be expressed in terms of the volume change as $dA = \frac{2dV_l}{r}$. Substitution of the last relation to eq. (2.5) gives

$$\begin{aligned} d\mathcal{S}_{\text{tot}} = &\left(\frac{1}{T_g} - \frac{1}{T_g}\right)dU_g + \left(\frac{1}{T_l} - \frac{1}{T_s}\right)dU_l \\ &+ \sum_i \left(\frac{\mu_{i,g}}{T_g} - \frac{\mu_{i,s}}{T_s}\right)dN_{i,g} \\ &+ \sum_i \left(\frac{\mu_{i,l}}{T_l} - \frac{\mu_{i,s}}{T_s}\right)dN_{i,l} \\ &+ \left(\frac{P_g}{T_g} - \frac{P_l}{T_l} + \frac{2\sigma}{T_s r}\right)dV_l \\ &= 0 \text{ for equilibrium.} \end{aligned}$$

Now (*but only now!*) we can use the “all directions” trick and get the old results (2.2) and (2.4) for temperature and chemical potential

$$T_g = T_l = T_s, \tag{2.6}$$

$$\mu_{i,g} = \mu_{i,l} = \mu_{i,s} \tag{2.7}$$

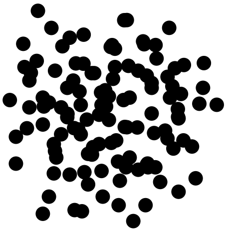
and a new one

$$\frac{P_g}{T_g} - \frac{P_l}{T_l} + \frac{2\sigma}{T_s r} = 0$$

which leads to the *Laplace equation*

$$\boxed{P_l = P_g + \frac{2\sigma}{r}. \qquad (2.8)}$$

Thus the pressure is higher inside the sphere (assuming $\sigma > 0$). This pressure difference provides the outward force to balance the tendency of the sphere to shrink because of surface tension (think about a balloon again).



For the future: we have overlooked an important issue: where should the surface be placed? For example: a liquid droplet does not change to gas abruptly, but the density decreases gradually. Where do we say is the surface of the droplet? More about this issue later on p. 55.

2.3 Gibbs phase rule

How many phases can be in equilibrium at once? Let us have n particle types and $i = 1, ..., n$ as the index of the molecule/atom type, and denote number of phases with p, with $k = 1, 2, .., p$ as the index of the phase. Intensive variables in each phase are P_k, T_k, $x_{1,k}$, $x_{2,k}$, $...x_{n,k}$, where mole fractions $x_{i,k}$ are defined as

$$x_i = \frac{N_i}{\sum\limits_i N_i}.$$

x_n is not a free variable if x_1, x_2, ... x_{n-1} are already set, because $x_n = 1 - \sum_{i=1}^{n} x_i$ (If we know that in a two-component system the mole fraction of sulphuric acid is 0.53, the mole fraction of water is necessarily 0.47). A complete list of independent variables reads

$k = 1$: T_1,P_1,$x_{1,1}$, $x_{2,1}$, ... $x_{n-1,1}$
$k = 2$: T_2,P_2,$x_{1,2}$, $x_{2,2}$, $...x_{n-1,2}$
.
.
.
$k = p$: T_p,P_p,$x_{1,p}$, $x_{2,p}$, $...x_{n-1,p}$

Total number of variables is thus $V_n = 2 \times p + (n-1)p = p(n+1)$.
Conditions which must be valid for all k,k' pairs are:

$T_k = T_{k'}$
$P_k = P_{k'}(\pm\frac{2\sigma}{r})$
$\mu_{i,k} = \mu_{i,k'}$ for every i

For pressures the $\frac{2\sigma}{r}$ term arises if the surface is curved, + sign corresponds to a convex surface of liquid, – sign a concave surface.
It is enough to require that in all the phases the temperature, pressure and chemical potentials for every component are equal to their value in the phase labelled k=1.

$$\begin{array}{lll}
\left.\begin{array}{l} \mu_{i,2} = \mu_{i,1} \\ \mu_{i,3} = \mu_{i,1} \\ \mu_{i,p} = \mu_{i,1} \end{array}\right\} & (p-1)n & \\
\left.\begin{array}{l} T_2 = T_1 \\ T_3 = T_1 \\ T_p = T_1 \end{array}\right\} & (p-1) & \left.\vphantom{\begin{array}{l} T \\ T \\ T \end{array}}\right\} \begin{array}{l} \text{number of} \\ \text{conditions} \\ C_n = \\ (n+2)(p-1) \end{array} \\
\left.\begin{array}{l} P_2 = P_1 \pm \frac{2\sigma_{1,2}}{r} \\ P_3 = P_1 \pm \frac{2\sigma_{1,3}}{r} \\ P_p = P_1 \pm \frac{2\sigma_{1,p}}{r} \end{array}\right\} & (p-1) &
\end{array}$$

For a solution to exist we have to have at least as many variables as conditions $V_n \geq C_n$

$$p(n+1) \geq (n+2)(p-1)$$

$$pn + p \geq pn - n + 2p - 2$$

$$0 \geq p - n - 2.$$

This is the *Gibbs phase rule*

$$\boxed{p \leq n + 2. \qquad (2.9)}$$

For a one-component system ($n = 1$) $p \leq 3$, in other words at most three phases can be simultaneously in equilibrium.

2.4 Phase diagrams

A phase diagram is obtained by drawing the phase equilibrium pressure P_e that is the same in all phases as a function of phase equilibrium temperature T which is also the same in all phases (for flat surface, one-component case): For all components i and all pairs of coexisting phases k and k' these P_e and T have to satisfy

$$\mu_{i,k}(P_e, T) = \mu_{i,k'}(P_e, T).$$

The point marked with TP in Fig. 2.5 is the *triple point.* All the phases allowed by the Gibbs phase rule *co-exist.* C is the *critical point.* If $T > T_c$, gas and liquid are not distinguishable as different phases. Vapour that is in equilibrium with liquid or solid is called *saturated vapour* (or equilibrium vapour). The pressure of this vapour, P_e, is the saturation vapour pressure (often misleadingly shortened to “vapour pressure”) or equilibrium vapour

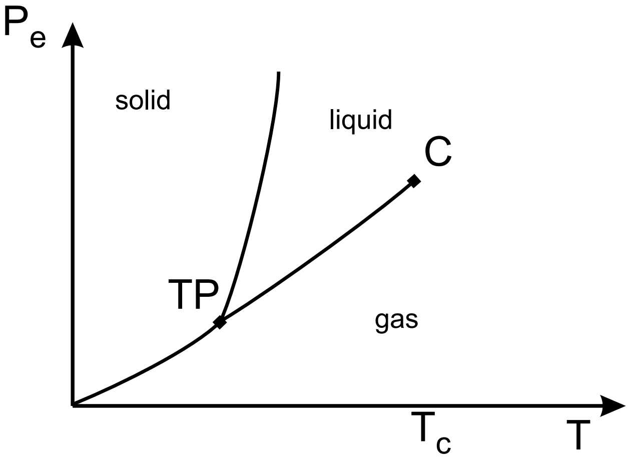


Fig. 2.5. Phase diagram in one component system.

pressure. If the pressure of vapour is higher than P_e, the vapour would like to turn to liquid. Why does it always not? The answer to this requires the concept of free energies and the way the transformation happens is called nucleation.

2.5 Saturation ratio and activities

Although the theory is applicable to any first-order phase transition, the main examples of this book concern gas-liquid transition. Liquid and gas phase activities, and the saturation ratio are concepts used to describe how far from the equilibrium state the vapour phase is when in contact with liquid. It is important to understand the definitions of the concepts well to avoid confusion when working with gas-liquid (or liquid-gas) nucleation.

2.5.1 Pure liquids

For a one-component system, the saturation ratio is defined as

$$S = P_g / P_e^p,$$

where P_g is the actual partial vapour pressure of component and $P_e^p = P_e^p(T)$ is the saturation vapour pressure over a flat surface of pure liquid (superscript ^{p} refers to pure compound).

NOTE: Saturation vapour pressure is a temperature-dependent property of the liquid! The liquid determines how dense a vapour should be above its surface in an equilibrium situation.

If there are more molecules/atoms in the vapour than equilibrium would allow, the vapour is *supersaturated* $S > 1$. *Supersaturation* $S - 1$ is often used instead of S. Relative humidity is defined as $RH = S_w \times 100\%$, and relative acidity as $RA = S_a \times 100\%$. Saturation means $RH = 100\% \Leftrightarrow S_w = 1$ and water has equilibrium vapour pressure. If $S < 1$ and there is a liquid pool present, liquid evaporates until there is none left (e.g. drying the laundry), or saturation is reached, and $S = 1$ (drying laundry in a poorly ventilated bathroom). If $S > 1$, vapour condenses if it is possible. This requires

- liquid pool present
- other surfaces to condense on available (macroscopic, like glasses or windows or microscopic, like small dust particles)

otherwise the excess molecules are trapped in the vapour which tries to nucleate.

Saturation vapour pressure is a very strong function of temperature

$$P_e(T) \sim \exp[f(T)], \tag{2.10}$$

where $f(T)$ is an increasing function of temperature, typically a polynomial of T and/or $1/T$. Thus the amount of vapour that "fits" to the gas phase depends strongly on temperature. If the concentration of vapour molecules in the room stays constant, but the temperature rises, the saturation ratio goes rapidly down. This can be seen by measuring RH in a sauna (doors and windows closed) when the temperature is rising/dropping!

2.5.2 Liquid solution

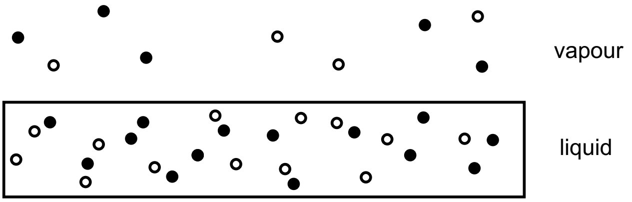
For mixtures, the saturation vapour pressure of component i is expressed as

$$P_{i,e}(x_i, T) = \Gamma_i(x_i, T) x_i P^p_{i,e}(T),$$

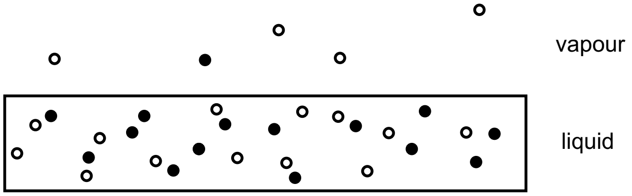
where x_i is the mole fraction of i in the liquid and $\Gamma_i(x_i, T)$ is the *activity coefficient.* Since only fraction x_i of the molecules in the liquid are of type i, also in the saturated vapour the fraction of these molecules is x_i if all the molecules escape to the vapour equally easily. This is the case in the ideal mixture, where the activity coefficient is unity, $\Gamma_i = 1$. In a non-ideal mixture the activity coefficient $\Gamma_i(x_{i,l}, T) \neq 1$ describes the difference in interaction between different types of molecules: some of them are more/less bound to the liquid solution than to pure liquid. *The liquid phase activity* is defined as

$$\mathcal{A}_{i,l} \equiv \frac{P_{i,e}(x_{i,l}, T)}{P^p_{i,e}(T)} = \Gamma_i x_i.$$

For a mixture, the *saturation ratio* S_i measures how saturated (close to equilibrium) the vapour i is with respect to the mixed liquid surface



Ideal liquid solution



Non-ideal solution: Black molecules stay in liquid

Fig. 2.6. Schematic figure of molecular composition of vapour and liquid in ideal (top, $x_{i,g} = x_{i,l}$) and non-ideal (bottom, $x_{i,g} \neq x_{i,l}$) solutions.

$$S_i \equiv \frac{P_{i,g}}{P_{i,e}(x_{i,l},T)} = \frac{P_{i,g}}{P^p_{i,e}(T)\mathcal{A}_{i,l}},$$

whereas the gas phase activity

$$\mathcal{A}_{i,g} = \frac{P_{i,g}}{P^p_{i,e}(T)}$$

measures how saturated the vapour is with respect to pure liquid i. Saturation ratio and gas phase activity are related through

$$S_i = \frac{\mathcal{A}_{i,g}}{\mathcal{A}_{i,l}(x_{i,l})}.$$

Tables 2.1 and 2.2 summarize the definitions of activities and saturation ratios. For the one-component case gas phase activity and saturation ratio are identical $\mathcal{A}_g = S = P/P^p_e(T)$, and liquid phase activity is identically equal to one $\mathcal{A}_l = 1$. [2]

---

[2] *NOTE: Sometimes in the literature the terms saturation ratio and gas phase activity are used exactly in the opposite way compared to this book. This unsettled terminology is very unfortunate and confusing. It is important to keep in mind the physics: one of them describes the saturation with respect to pure liquid, and the other with respect to mixture. The context usually tells which terminology is used. If an experimentalist tells you that they adjusted their saturation ratio to be 7 and no other information apart from temperature is given, it is most likely our gas phase activity, because otherwise they would state with respect to which liquid*

Table 2.1. Summary of definitions for saturation activities and saturation ratios.

	pure compound	mixture
vapour in equilibrium with liquid	saturation vapour pressure P_e^p	saturation vapour pressures $P_{i,e}$ liquid phase activities $\mathcal{A}_{i,l} = P_{i,e}/P_{i,e}^p$ activity coefficients $\Gamma_i = \mathcal{A}_{i,l}/x_{i,l}$
ambient vapour	vapour pressure P_g Saturation ratio $S = P_g/P_e^p$ gas phase activity $\mathcal{A}_g = S$	vapour pressures $P_{i,g}$ gas phase activities $\mathcal{A}_{i,g} = P_{i,g}/P_{i,e}^p$ saturation ratios $S_i = P_{i,g}/P_{i,e} = \mathcal{A}_{i,g}/\mathcal{A}_{i,l}$

If the activity coefficient is lower than one, $\Gamma_i(x_{i,l}, T) < 1$, molecules of i have stronger attractive interaction in the mixture than in the pure liquid. Typically $\mathcal{A}_{i,l}(x_{i,l}) < 1$ since evidently the mole fraction is less than one, $x_{i,l} < 1$, and activity coefficients $\Gamma_i(x_{i,l})$ are normally less or equal to one, and thus the vapour can be supersaturated $S_i > 1$ with respect to mixture with mole fraction $x_{i,l}$ although it is subsaturated with respect to pure liquid i, $\mathcal{A}_{i,g} < 1$. A good example is sulphuric acid-water solution: even when both of them are subsaturated with respect to pure acid/water they can be highly supersaturated with respect to H_2SO_4-H_2O solution. The potential energy due to molecular binding is much higher between a water molecule and a sulphuric acid molecule than between two water or two acid molecules. In chemistry words this is due to the fact that sulphuric acid is a proton donor (acid) and water can act as proton acceptor (base), and thus they form strong hydrogen bonds.

Table 2.2. Summary of nominators and denominators of activities and saturation ratio.

denominator:saturation vapour pressure over	nominator	
	saturation vapour pressure	ambient vapour pressure
pure compound	liquid phase activity $\mathcal{A}_{i,l}$	gas phase activity $\mathcal{A}_{i,g}$
ideal mixture	activity coefficient Γ_i	-
real mixture	1	saturation ratio S_i

---

composition. Our gas saturation ratio alone does not tell how many molecules i there are in the vapour, we need to know also the composition of the liquid mixture. Our gas phase activity is in that sense more informative than saturation ratio, we need to know only the saturation vapour pressure of the pure component to calculate the partial vapour pressure or vapour concentration of i. But saturation ratio, on the other hand, tells us immediately on what side and how close to equilibrium the vapour is in that specific situation.

2.6 Conventional form of the gas-liquid equilibrium conditions

We want to transform the spherical surface phase equilibrium conditions (2.6), (2.7) and (2.8)

$$T_l = T_g$$

$$P_l = P_g + \frac{2\sigma}{r}$$

$$\mu_{i,l}(P_l, x_{i,l}) = \mu_{i,g}(P_g, x_{i,g})$$

to a more practical form in the case of gas-liquid equilibrium.

NOTE: Generally mole fractions in the vapour and liquid are different $x_{i,l} \neq x_{i,g}$.

In a multicomponent system we have to use one of the Maxwell equations (which will be derived later on p. 47) to manipulate chemical potentials:

$$\left(\frac{\partial \mu_i}{\partial P}\right)_{x_i,T} = \left(\frac{\partial V}{\partial N_i}\right)_{P,T,N_{j\neq i}}.$$

The partial molecular volume v_i is defined as

$$v_i \equiv \left(\frac{\partial V}{\partial N_i}\right)_{P,T,N_{j\neq i}}, \tag{2.11}$$

and it measures how much the volume increases when we add one molecule of type i to the system at constant temperature and pressure. For pure liquids, the partial molecular volume is simply the volume per molecule $v = V/N$.

NOTE: The quantities kept constant on either side of the Maxwell equation are not *the same!*

Partial molecular volumes can be calculated if we know the density as a function of composition $\rho(x_i)$. Using the fact that volume V and particle number N_i are extensive quantities we can derive a relation between the partial molecular volumes, numbers of molecules in the system and the volume of the system: If we put λ systems together the volume is multiplied by λ

$$V(\lambda N_i) = \lambda V(N_i).$$

We take the derivative of this equation with respect to λ

$$\left(\frac{\partial V(\lambda N_i)}{\partial \lambda}\right) = \sum_i \left(\frac{\partial V}{\partial(\lambda N_i)}\right) N_i = V(N_i)$$

and set $\lambda = 1$, we get

$$\sum_i \left(\frac{\partial V}{\partial N_i}\right) N_i = V,$$

which in terms of the partial molecular volumes reads

$$\boxed{\sum N_i v_i = V. \qquad (2.12)}$$

NOTE 1: This derivation goes just like the derivation of the fundamental equation on p. 11.

NOTE 2: It follows from eq. (2.12) that

$$v_i \equiv \left(\frac{\partial V}{\partial N_i}\right)_{N_j,T} = v_i + \sum_k N_k \left(\frac{\partial v_k}{\partial N_i}\right)_{N_j,T}$$

which means we must always have

$$\sum_k N_k \left(\frac{\partial v_k}{\partial N_i}\right)_{N_j,T} = 0.$$

This is one way of checking that you have correct formulae for partial molar volumes in your computer code.

Our Maxwell equation can be written as

$$\boxed{d\mu_i = v_i dP \quad \text{when } x_i \text{ and } T \text{ are kept constant.} \qquad (2.13)}$$

Take the integral of the liquid chemical potential (keeping $x_{i,l}, T$ constant):

$$\int_{P_g}^{P_l} d\mu_{i,l} = \int_{P_g}^{P_l} v_{i,l} dP.$$

Integration on the left-hand side yields

$$\mu_{i,l}(P_l, x_{i,l}) = \mu_{i,l}(P_g, x_{i,l}) + \int_{P_g}^{P_l} v_{i,l} dP,$$

and if the liquid is incompressible $v_{i,l}$ does not depend on P (when $x_{i,l}$ is kept constant) and we can perform the remaining integral to get

$$\mu_{i,l}(P_l, x_{i,l}) = \mu_{i,l}(P_g, x_{i,l}) + v_{i,l}(P_l - P_g).$$

Now we use the equilibrium condition for chemical potentials,
eq. (2.7), $\mu_{i,l}(P_l, x_{i,l}) = \mu_{i,g}(P_g, x_{i,g})$ to get

$$\mu_{i,g}(P_g, x_{i,g}) = \mu_{i,l}(P_g, x_{i,l}) + v_{i,l}(P_l - P_g).$$

Next we move the chemical potentials to the same side of the equation and use the pressure equilibrium condition (Laplace equation 2.8) $P_l = P_g + \frac{2\sigma}{r}$ and get

$$\mu_{i,l}(P_g, x_{i,l}) - \mu_{i,g}(P_g, x_{i,g}) = -v_{i,l}(P_l - P_g) = -\frac{2\sigma v_{i,l}}{r}.$$

Now we introduce a conventional definition

$$\boxed{\Delta\mu_i \equiv \mu_{i,l}(P_g, x_{i,l}) - \mu_{i,g}(P_g, x_{i,g}) \qquad (2.14)}$$

and get the *Kelvin equation*

$$\boxed{\Delta\mu_i + \frac{2\sigma v_{i,l}}{r} = 0 \quad \text{for each i.} \qquad (2.15)}$$

$\Delta\mu_i$ is often misleadingly called the chemical potential difference between vapour and liquid. In equilibrium, chemical potential differences between phases are of course equal to *zero*! But in $\Delta\mu_i$ the chemical potential of the liquid is taken at *vapour* pressure, not at *liquid* pressure.

If we want to calculate the properties of equilibrium droplet using Kelvin equation (2.15) we know

$\sigma = \sigma(T, x_i)$ from experimental data
$v_{i,l} = v_{i,l}(T, x_i)$ from experimental liquid density data

We still have to convert $\Delta\mu_i$ to something measurable. First study the liquid chemical potential and use eq. (2.13) $d\mu_{i,l} = v_{i,l}dP$ and incompressibility again to get

$$\begin{aligned} \mu_{i,l}(P_g, x_{i,l}) &= \mu_{i,l}(P_x, x_{i,l}) + \int_{P_x}^{P_g} v_{i,l}dP \\ &= \mu_{i,l}(P_x, x_{i,l}) + v_{i,l}(P_g - P_x) \end{aligned} \qquad (2.16)$$

where P_x is an (so far) arbitrary liquid pressure.

We manipulate the chemical potential of the vapour by assuming that the mixture of vapours is an *ideal mixture*. This means that each component behaves as if it was alone with total pressure equal to the partial pressure of that component, $P_{i,g} = x_{i,g}P_g$. Let $\mu^p_{i,g}(P)$ and $v^p_{i,g}(P)$ be the chemical potential and partial molecular volume of an independent (pure) vapour i at pressure P. In this case

$$\mu_{i,g}(P_g, x_{i,g}) = \mu^p_{i,g}(P_g x_{i,g}) = \mu^p_{i,g}(P_{i,g}) = \mu^p_{i,g}(P'_{i,x}) + \int_{P'_{i,x}}^{P_{i,g}} v^p_{i,g}dP, \quad (2.17)$$

where $P'_{i,x}$ is so far arbitrary vapour pressure.

Now we select liquid pressure P_x and vapour pressure $P'_{i,x}$ so that component i of the vapour is in equilibrium with the liquid in a flat surface case, $\mu_{i,l}(P_x, x_{i,l}) = \mu^p_{i,g}(P'_{i,x})$. The other components $j \neq i$ are not necessarily in equilibrium at the same time. Since we have selected equilibrium over flat surface, the vapour pressure must be that of the saturated vapour $P'_{i,x} = P_{i,e}(x_{i,l})$ and the total vapour pressure $P_{\text{tot,e}}(x_{i,l}) \equiv \sum_i P_{i,e}(x_{i,l})$ must be equal to the liquid pressure, $P_x = P_{\text{tot,e}}(x_{i,l})$.

Now we can calculate $\Delta\mu_i$ by subtracting eq. (2.17) from eq. (2.16)

$$\begin{aligned}\Delta\mu_i &= \mu_{i,l}(P_g, x_{i,l}) - \mu_{i,g}(P_g, x_{i,g}) \\ &= \mu_{i,l}(P_x, x_{i,l}) + v_{i,l}(P_g - P_x) \\ &- \mu^p_{i,g}(P_{i,e}(x_{i,l})) - \int_{P_{i,e}}^{P_{i,g}} v^p_{i,g} dP \\ &= v_{i,l}(P_g - P_{\text{tot},e}(x_{i,l})) - \int_{P_{i,e}(x_{i,l})}^{P_{i,g}} v^p_{i,g} dP.\end{aligned}$$

If *(but only if)* the vapour is an ideal gas (as well as an ideal mixture) the ideal gas law gives the partial molecular volume in the vapour

$$P_i V = kTN_i \Rightarrow v^p_{i,g} = V/N_i = \frac{kT}{P} \tag{2.18}$$

and using the definitions of saturation ratio and activities (p. 24) we get

$$\int_{P_{i,e}(x_{i,l})}^{P_{i,g}} v^p_{i,g} dP = \int_{P_{i,e}(x_{i,l})}^{P_{i,g}} \frac{kT}{P} dP = kT \ln \frac{P_{i,g}}{P_{i,e}(x_{i,l})} = kT \ln \frac{\mathcal{A}_{i,g}}{\mathcal{A}_{i,l}} = kT \ln S_i. \tag{2.19}$$

Thus for an ideal gas

$$\Delta\mu_i = v_{i,l}(P_g - P_{\text{tot},e}(x_{i,l})) - kT \ln \frac{\mathcal{A}_{i,g}}{\mathcal{A}_{i,l}}.$$

Usually $kT \ln \frac{\mathcal{A}_{i,g}}{\mathcal{A}_{i,l}}$ is much larger than $v_{i,l}(P_g - P_{\text{tot},e}(x_{i,l}))$ as can been seen by the following estimate:
$T \sim 300\text{K}$, $k = 1.38 \cdot 10^{-23}$, $kT \sim 4 \cdot 10^{-21}$ J
$P_g - P_{\text{tot},e} \sim 10^4$ Pa (RH=500 %, T=298K),
$v_{i,l} \sim 1/\rho_l \sim 10^{-30}\text{m}^3$,
$v_{i,l}(P_g - P_{\text{tot},e}) \sim 10^{-26}$ J $\ll 4 \cdot 10^{-21}$ J $\sim kT$
and we have for ideal mixture of ideal gases and incompressible liquid a simple form

$$\boxed{\Delta\mu_i = -kT \ln \frac{\mathcal{A}_{i,g}}{\mathcal{A}_{i,l}(x_{i,l})} = -kT \ln S_i.} \tag{2.20}$$

Combining equations (2.17) and (2.18) and performing the integral in the same way as in eq. (2.19) we get the general result for the pressure dependence of the chemical potential of an ideal gas

$$\mu^p_{i,g}(P_{i,g}) = \mu^p_{i,g}(P'_{i,x}) + kT \ln \frac{P_{i,g}}{P'_{i,x}}. \tag{2.21}$$

2.7 Summary of equilibrium conditions for spherical droplets

Now we have all the required pieces in terms of measurable quantities to use the Kelvin equation (2.15) to answer two kinds of equilibrium questions :

1. If we have a vapour with known partial pressures ($\mathcal{A}_{1,g}, \mathcal{A}_{2,g}, ..., \mathcal{A}_{n,g}$ are given) what kind of a droplet is in equilibrium with it ? We have n Kelvin equations (2.15), one for each component, but each of them contains $2\sigma/r$ which is independent of component i. We can solve this i-independent combination as
$$\frac{2\sigma}{r} = \frac{\Delta\mu_i}{v_{i,l}}$$
from each equation and set them equal to each other to get $n-1$ equations
$$\frac{\Delta\mu_2}{v_{2,l}} = \frac{\Delta\mu_1}{v_{1,l}} \Rightarrow \frac{kT\ln\dfrac{\mathcal{A}_{2,g}}{\mathcal{A}_{2,l}(x_{2,l})}}{v_{2,l}(x_{2,l})} = \frac{kT\ln\dfrac{\mathcal{A}_{1,g}}{\mathcal{A}_{1,l}(x_{1,l})}}{v_{1,l}(x_{1,l})} \qquad (2.22)$$
$$\vdots$$
$$\frac{\Delta\mu_n}{v_{n,l}} = \frac{\Delta\mu_1}{v_{1,l}} \Rightarrow \frac{kT\ln\dfrac{\mathcal{A}_{n,g}}{\mathcal{A}_{n,l}(x_{n,l})}}{v_{n,l}(x_{n,l})} = \frac{kT\ln\dfrac{\mathcal{A}_{1,g}}{\mathcal{A}_{1}(x_{1,l})}}{v_{1,g}(x_{1,l})} \qquad (2.23)$$
which can be used to solve $n-1$ mole fractions $x_{1,l}...x_{n-1,l}$. The last mole fraction is given by
$$x_{n,l} = 1 - \sum_{i=1}^{n-1} x_{i,l}.$$
and the radius of the droplet is obtained from
$$r = \frac{2\sigma v_{i,l}}{\Delta\mu_i} = \frac{2\sigma v_{i,l}(x_{i,l})}{kT\ln(\mathcal{A}_{i,g}/\mathcal{A}_{i,l})} \qquad (2.24)$$
for any i. A good way of checking that the composition is correctly solved is to check that r is really the same if we use different component i in eq. (2.24).
2. We have a droplet with radius r and composition $x_{i,l}$. What is the equilibrium pressure of component i over this surface? Equation
$$kT\ln\frac{P_{i,g}}{P_{i,e}(x_{i,l})} = \frac{2\sigma v_{i,l}}{r}$$
gives

$$\begin{aligned} P_{i,g} = P_{i,e}(x_{i,l}) \exp\left(\frac{2\sigma v_{i,l}}{rkT}\right) &= \mathcal{A}_{i,l}(x_{i,l}) P^{p}_{i,e}(T) \exp\left(\frac{2\sigma v_{i,l}}{rkT}\right) \\ &= \mathit{\Gamma}_i x_{i,l} P^{p}_{i,e}(T) \exp\left(\frac{2\sigma v_{i,l}}{rkT}\right), \end{aligned} \tag{2.25}$$

where the exponent term describes so-called Kelvin effect and $P_{i,e}(x_{i,l}) = \mathcal{A}_{i,l}(x_{i,l}) P^{p}_{i,e}(T) = \mathit{\Gamma}_i x_{i,l} P^{p}_{i,e}(T)$ is the saturation pressure over a flat surface. Kelvin effect is the increase of saturation vapour pressure due to increased curvature of the surface. It is easier for molecules to escape a curved surface because they are more weakly bound to their neighbours, and thus the saturation vapour pressure is higher.

2.8 Van der Waals fluid

To give a concrete example of how the equation of state, together with equilibrium conditions, can be used to find phase co-existence in practice, we study a van der Waals fluid. Van der Waals equation is the simplest often used equation of state that predicts phase separation:

$$\big(P + \frac{a}{v^2}\big)(v - b) = kT,$$

where the molecular volume is $v = \frac{V}{N}$. Van der Waals equation can be rearranged as

$$P = \frac{kT}{v - b} - \frac{a}{v^2}.$$

Here b is the smallest possible volume per molecule of the atom/molecule (hard sphere radius). Now we assume atoms/molecules are not point-like as in the ideal gas. v is the volume an atom/molecule on average occupies in the vapour/liquid, parameter a is connected to the attraction between molecules. The molecules are attracted to each other and the “outward” pressure is smaller than in the ideal gas (non-attracting), and molecules are within the attraction distance with a probability $\sim 1/v^2$.

We draw P as a function of v at a fairly low constant temperature T in Fig. 2.7 and notice that same P occurs with two or three different volumes v. What does that mean?

First remember the stability condition (p. 18):

$$K_T = -\frac{1}{V}\big(\frac{\partial V}{\partial P}\big)_{T,N} > 0 \Rightarrow \big(\frac{\partial P}{\partial V}\big) < 0,$$

so P has to decrease with V and points like B$'$ are completely unstable. Systems at points A, B and C have lower V, higher density than at points

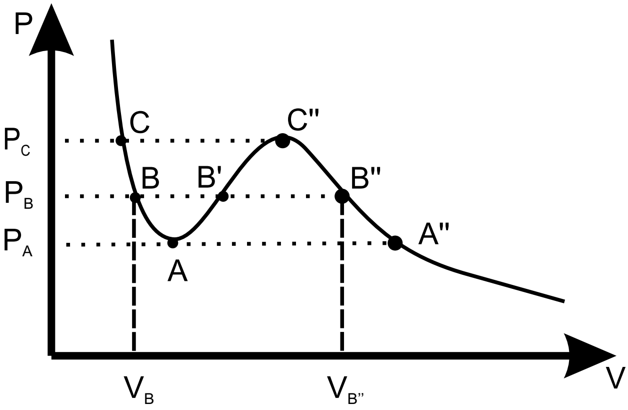


Fig. 2.7. Pressure as a function of molecular volume v according to the van der Waals equation of state at a fairly low temperature. See text for explanation of the points marked with letters.

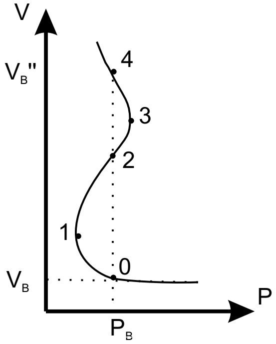


Fig. 2.8. Molecular volume v dependence on pressure P according to the van der Waals equation of state at a fairly low temperature. v is not a function of P because one P corresponds to multiple values of v (but P is a function of v). See text for information about the points marked with numbers.

A$''$, B$''$ and C$''$; A, B and C are liquid, A$''$, B$''$ and C$''$ are gas. For $P > P_\mathrm{C}$ only liquid phase exists and for $P < P_\mathrm{A}$ only gas phase exists.

We would like to know at which pressure gas and liquid are in equilibrium, in which case $P_\mathrm{B} = P''_\mathrm{B} = P_e$ is the saturation vapour pressure. Phase coexistence conditions tell us this. For a flat surface (p. 17):

$P_g = P_l$ on a line perpendicular to P-axis,
$T_g = T_l$ on a T-constant curve, and
$\mu_g = \mu_l$ gives more information.

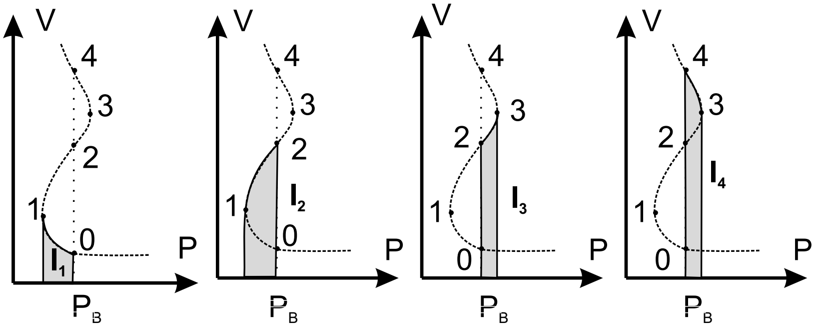


Fig. 2.9. Parts of the curve in Fig. 2.8 which correspond to well-defined function (cut from the points 1,2,3 and 4 shown also in figure 2.8), and the areas $I_1 - I_4$ underneath these curves.

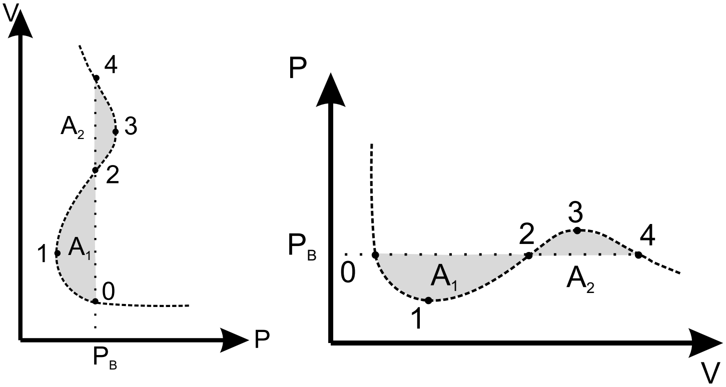


Fig. 2.10. The sum of areas shown in Fig. 2.9, $A_1 = I_2 - I_1$ and $A_2 = I_4 - I_3$, with the signs resulting from integration to positive and negative directions of the P-axis taken into account. The right-hand figure shows the situation in the coordinate system of Fig. 2.7.

We need the Gibbs-Duhem equation to convert the chemical potential condition to a practical form. The isothermal Gibbs-Duhem equation (1.9) (or Maxwell equation 2.13) for a one-component system reads $Nd\mu = VdP \Rightarrow d\mu = vdP$ which can be integrated over pressure to give

$$\mu_B'' = \mu_B + \int_{v_B}^{v_B''} vdP.$$

We have to express v as a function of P instead of P as a function of v (Fig. 2.7) to perform this integral. Fig. 2.8 shows the situation when we have swapped the roles of x and y-axes compared to Fig. 2.7 .

Now the molecular volume v is not a well-defined function of pressure P, since several values of v can be obtained with a single P. To perform the

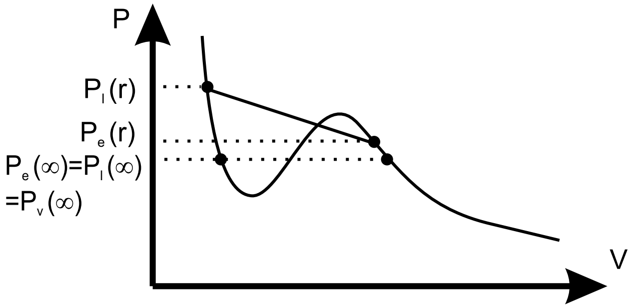


Fig. 2.11. Liquid pressure $P_l(r)$ and saturation vapour pressure $P_g(r)$ for a spherical droplet compared to the flat surface saturation vapour pressure $P_g(\infty)$.

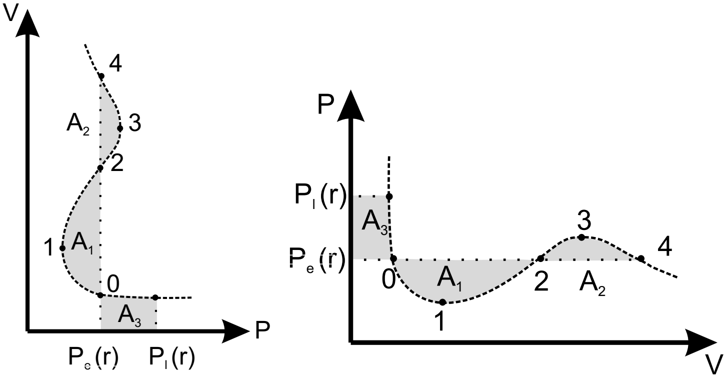


Fig. 2.12. Figure corresponding to Fig. 2.10, but for spherical surface. For equilibrium the sum of areas $A_2 + A_3$ must be equal to area A_1.

integral we have to divide the curve into parts where the molecular volume has an unique value with given pressure. The boundaries of these parts are shown in Fig. 2.8 as points number 0, 1, 2, 3 and 4. We integrate vdP in small parts: the first part 0→1, the integral gives $\int_0^1 vdP = -I_1$ where I_1 is the area marked in Fig. 2.9 (negative since we go to negative direction in P) part 1→2 gives $\int_1^2 vdP = I_2$, part 2→3 gives $\int_2^3 vdP = I_3$ and the final part 3→4 gives $\int_3^4 vdP = -I_4$. Fig. 2.10 gives the result when these four parts are added together with the signs taken into account. The equality of chemical potentials can be expressed as

$$\mu''_B = \mu_B + A_1 - A_2,$$

where areas $A_1 = I_2 - I_1$ and $A_2 = I_4 - I_3$ are shown in Fig. 2.10. So for the chemical potentials to be equal, the areas A_1 and A_2 have to be the same. This area-based method for finding the phase equilibrium is called the *Maxwell construction.*

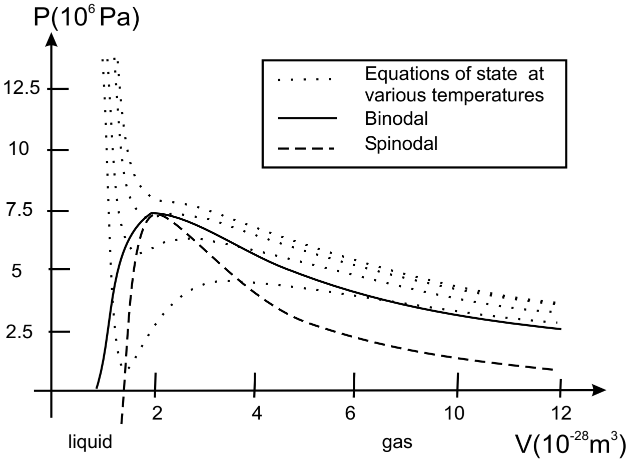


Fig. 2.13. Binodal and spinodal for van der Waals fluid with parameters corresponding to CO_2 ($a = 1.00813 \cdot 10^{-48}\mathrm{Nm}^4$ and $b = 7.140 \cdot 10^{-29}\mathrm{m}^3$). The curves are plotted in terms of molecular volume. Also curves showing pressure as a function of molecular volume according to the equation of state are shown for temperatures (top to bottom) 310K, 303K (critical temperature), 290K and 260K.

How does the picture look like for spherical droplets? The equilibrium condition (2.8) tells us that the liquid pressure is higher than the vapour pressure $P_l(r) = P_g(r) + \frac{2\sigma}{r} > P_e(r)$ and due to the Kelvin effect (2.25) the saturation vapour pressure is higher than for a flat surface $P_g(r) = \exp(\frac{2\sigma v_l}{rkT}) \cdot P_e$, with $P_e = P_g(\infty)$. A similar series of integrals can be performed as in the flat surface case, now from $P_l(r)$ to $P_g(r)$ and the conclusion is that, in equilibrium, areas $A_2 + A_3$ in Fig. 2.12 must be equal to area A_1.

Now we return to the flat surface case and study how temperature affects the phase equilibrium. A *binodal* is the curve formed by equilibrium points B and B$''$ satisfying $\mu_{\mathrm{B}} = \mu''_{\mathrm{B}}$ at different temperatures (Figures 2.13 and 2.14). If we plot points A and C$''$ for different temperatures we get a curve called *spinodal*, which restricts the forbidden area where the system is unstable. When temperature T increases the valley A becomes less deep and at $T = T_c$ it vanishes. With $T \geq T_c$ there is only one v for each P. T_c is the critical temperature above which gas and liquid are not separable phases. Spinodal and binodal meet at the highest point of both of these curves, and this point corresponds to the critical temperature T_c and pressure p_c above which liquid and vapour are not distinguishable phases. The critical temperature and pressure can be found by finding the conditions where the $P(v)$ curve has a point where its first and second derivatives vanish simultaneously.

NOTE: Binodal, spinodal and their relation to critical point are general features not restricted to the specific case of van der Waals liquid.

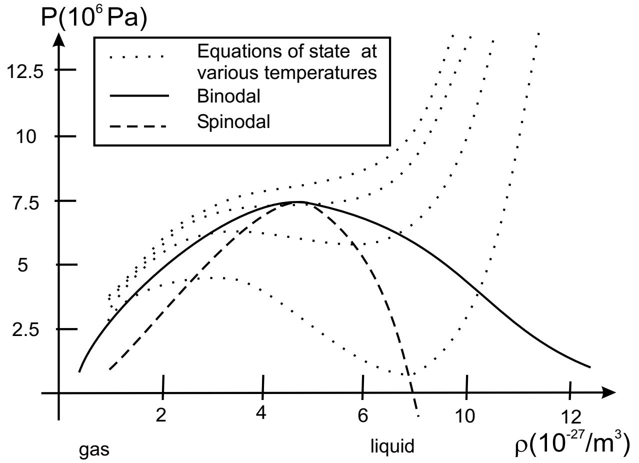


Fig. 2.14. Binodal and spinodal for van der Waals fluid with parameters corresponding to CO2 ($a = 1.00813 \cdot 10^{-48}\mathrm{Nm}^4$ and $b = 7.140 \cdot 10^{-29}\mathrm{m}^3$). The curves are plotted in terms of liquid density. Also curves showing pressure as a function of liquid density according to the equation of state are shown for temperatures (top to bottom) 310K, 303K (critical temperature), 290K and 260K.

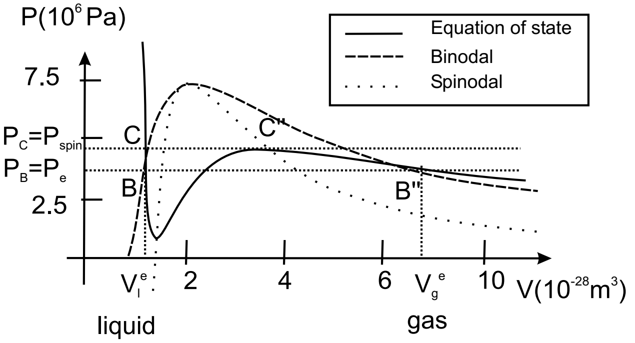


Fig. 2.15. Pressure as a function of molecular volume v according to the van der Waals equation of state for CO2 at 260K. See caption to Fig. 2.13 for the parameters. The binodal and spinodal are also shown, as well as equilibrium vapour pressure and spinodal pressure.

What happens if we start to slowly increase the vapour pressure of a gas phase system at a constant temperature, starting at the right-hand edge of Fig. 2.15, with pressure lower than saturation vapour pressure P_e. The system follows the curve toward B$''$ but does not jump to B at B$''$. Instead it follows the curve from B$''$ upward toward C$''$. It is still in a metastable equilibrium, energetically it should jump to the curve above point B, but it is trapped on the gas side of the curve. When the pressure is increased beyond equilibrium vapour pressure P_e, the equilibrium molecular volume jumps suddenly from

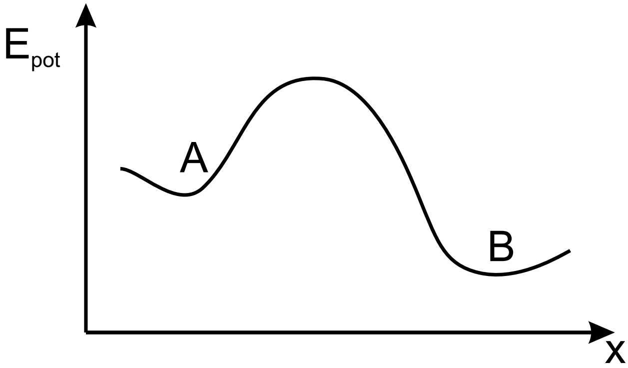


Fig. 2.16. Potential energy surface with local and global minima.

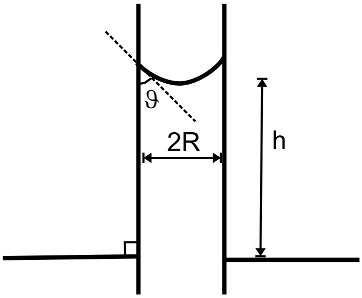
equilibrium vapour value v_g^e to equilibrium liquid value v_l^e. Jumps like this are typical for *first-order phase transitions* (see p. 128). The fluctuations in density ($\rho = 1/v$) are not big enough to transfer the gas to liquid and we have a supersaturated vapour. If the pressure increases above the spinodal pressure $P_C = P_{\text{spin}}$, the vapour-liquid transition happens immediately. When the system is between B$''$ and C$''$ it can undergo a transition if we leave it for a long time or disturb it, for example by shaking. If undisturbed, local fluctuations can form small liquid droplets, but the whole system does not transform to a liquid. The formation of local areas of the stable phase (liquid in this case) in a unstable phase (gas in this case) is *nucleation*: small nuclei of the stable phase form. If we start with liquid at pressure P_C in Fig. 2.15 and lowered it below P_e we have a similar situation: the system should change phase and become vapour, but it is trapped into the liquid phase. The situation in nucleation is analogous to a local minimum situation in potential energy shown in Fig. 2.16. If a ball is at point A, B has a clearly lower energy, but how to get there? There is a barrier (or mountain, or hill) between A and B. B is a global minimum, A is only a local one. When pressure is increased for binodal to spinodal, the barrier gets lower and at spinodal there is not barrier anymore. Next we will find out what is the type of energy in phase transition that forms a barrier.

Problems

2.1. Use the Laplace equation and equation for hydrostatic pressure to show that in a capillary tube the liquid rises to level h where

$$h = \frac{2\sigma \cos \vartheta}{m\rho g R},$$

where g is the gravitation acceleration, ρ is the liquid number density, m is the molecular mass, σ is the surface tension, ϑ is the contact angle between liquid and tube wall and R is the radius of the tube (You can take the liquid surface to be part of a sphere, and h to be the "average" height).



2.2. If you know
A) the number density
B) the mass density of a liquid as a function of
a) mole fractions $x_i = N_i / \sum_i N_i$
b) mass fraction $x_{i,m} = N_i m_i / \sum_i N_i m_i$
derive the expression for partial molecular volume.

2.3. Use the Gibbs-Duhem equation to derive a consistency condition that has to be satisfied by the activity coefficients in a two-component system.

2.4. Derive expressions for the critical point temperature, pressure and molecular volume of a van der Waals fluid.

2.5. For a van der Waals fluid modelling nitrogen the parameters are
$a = 3.65586525$ bar dm^6/mol^2
$b = 0.04282639$ dm^3/mol
a) Plot three isotherms, two below and one above critical temperature in (P, v)-coordinate system
b) plot the spinodal and the binodal.

3

Formation free energy

So far we have studied isolated systems : U, V, N_i are constant. Equilibrium is determined by maximum of entropy $\mathcal{S} = \mathcal{S}_{\text{max}}$. The maximum is found in respect to some extra parameter(s) $x(, y, ...)$ while keeping $U(x, ...)$, $V(x, ...)$, $N_i(x, ...)$ constant. x can be for example the position of a dividing wall as in Fig. 3.1.

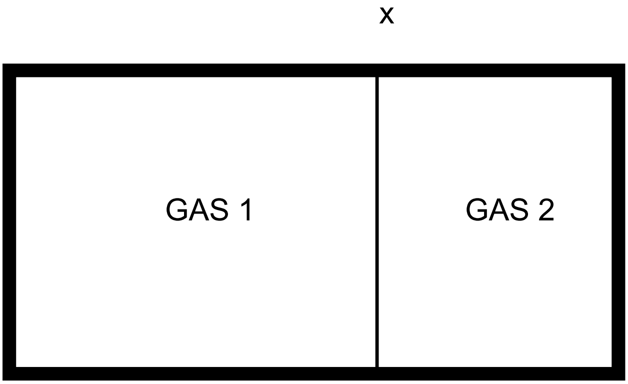


Fig. 3.1. Isolated system with a dividing wall at position x separating two types of gases.

Insulated rigid box keeps U_{tot}, V_{tot} and $N_{i,\text{tot}}$ constant.

$$U_{\text{tot}} = U_1 + U_2$$

$$N_{i,\text{tot}} = N_{i,1} + N_{i,2}$$

$$V_{\text{tot}} = V_1 + V_2.$$

By maximising $\mathcal{S}$ with respect to x we find the equilibrium position of the dividing wall. A reversible process in a system with U_{tot}, V_{tot}, $N_{i,\text{tot}}$ kept constant means also constant entropy since $d\mathcal{S}_{\text{tot}} = 0$, the system is always in equilibrium, and $\mathcal{S}_{\text{tot}}$ keeps having its maximum value.

What if we have some other set of constants?
Intensive variables P, T, μ_i can be kept constant by connecting the system to a bath: A bath is an equilibrium system much bigger than our system. The intensive properties of the bath $(P_0, T_0, \mu_{i,0})$ do not change even if the system exchanges heat, volume and/or particles with the bath. The extensive properties (V_0, $N_{i,0}$, $\mathcal{S}_0, U_0$) of the bath can change. The system is so small that anything coming out of it or going into it is a drop in the ocean for the bath.

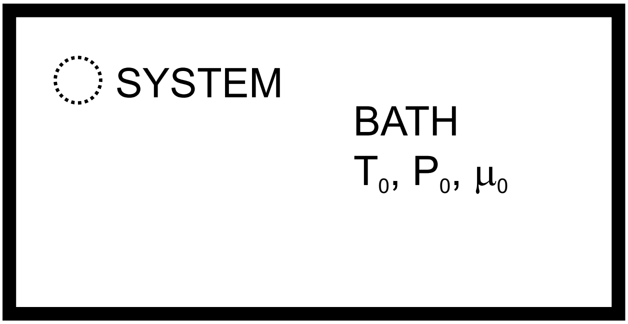


Fig. 3.2. The combination of the system and the bath is isolated. The system is much smaller than the bath.

Heat bath: Exchanges heat with the system, heat flows in and out so that the temperature of the system stays constant and equal to that of the bath in quasi-static processes. In real irreversible processes the temperature of the system is not necessarily well defined or unique at all times.

Pressure bath: Exchanges volume work with the system. The volume of the system changes so that the pressure stays constant and equal to that of the bath in quasi-static processes. In irreversible processes the pressure of the system is not necessarily well defined or unique.

Particle bath: Exchanges particles with the system so that the chemical potentials of the system stay constant and equal to those in the bath in reversible processes. Again in irreversible processes the chemical potential of the system is not always well defined.

NOTE: In the bath $T_0, P_0, \mu_{i,0}$ are always well defined and thus all the processes in the bath are reversible. This is a crucial point in what follows

The combination of system and bath is an isolated system. $\mathcal{S}$ is entropy of the system and $\mathcal{S}_0$ of the bath, so total entropy is $\mathcal{S}_{\text{tot}} = \mathcal{S} + \mathcal{S}_0$. According to the second law of thermodynamics (1.4) all possible processes occur so that entropy increases $d\mathcal{S}_{\text{tot}} \geq 0$ ($d\mathcal{S}_{\text{tot}} = 0$ for reversible processes only).
In terms of system and bath entropies this reads

$$d\mathcal{S}_{\text{tot}} = d\mathcal{S} + d\mathcal{S}_0 \geq 0.$$

The bath always undergoes reversible changes:

$$\text{đ}Q_0 = T_0 d\mathcal{S}_0,$$

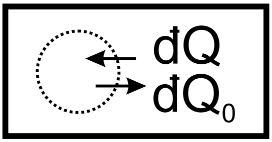
$$\text{đ}W_0 = P_0 dV_0.$$

Using the reversible form for the heat that entered the bath we can write the change of total entropy as

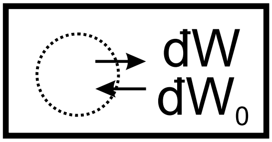
$$d\mathcal{S}_{\text{tot}} = d\mathcal{S} + d\mathcal{S}_0 = d\mathcal{S} + \frac{\text{đ}Q_0}{T_0} = d\mathcal{S} - \frac{\text{đ}Q}{T_0}. \tag{3.1}$$

Conservation laws say that everything that left the system entered the bath, and vice versa:

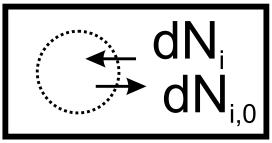
- Heat balance: heat that entered the system $\text{đ}Q$ left the bath. Heat that entered the bath is then $\text{đ}Q_0 = -\text{đ}Q$



- Work done by the system $\text{đ}W$ enters the bath.
  Work done by the bath is $\text{đ}W_0 = -\text{đ}W$



- Total volume is conserved:
  Volume change of the system dV.
  Volume change of the bath is $dV_0 = -dV$
- Particles that entered the system left the bath $dN_i = -dN_{i,0}$ but also the energy they carried must balance:
  $\mu_i dN_i = -\mu_{i,0} dN_{i,0}$



First law for the system reads

$$dU = \text{đ}Q - \text{đ}W + \sum_i \mu_i dN_i.$$

We solve the heat $\text{đ}Q$ entering the system from the first law

$$\text{đ}Q = dU + \text{đ}W - \sum \mu_i dN_i$$

and use the conservation laws above to express the changes in the system properties in terms of the changes in the bath properties

$$\text{đ}Q = dU - \text{đ}W_0 + \sum \mu_{i,0} dN_{i,0}.$$

Then we use reversible forms for the changes in bath properties

$$đQ = dU - P_0 dV + \sum \mu_{i,0} dN_{i,0}$$

and the conservation laws again to return to the system properties

$$đQ = dU + P_0 dV - \sum \mu_{i,0} dN_i.$$

When we substitute this to the second law (eq. 3.1) we get

$$d\mathcal{S}_{\mathrm{tot}} = d\mathcal{S} - \frac{dU + P_0 dV - \sum_i \mu_{i,0} dN_i}{T_0} \geq 0.$$

Now we multiply this by $T_0 \neq 0$:

$$T_0 d\mathcal{S} - dU - P_0 dV + \sum_i \mu_{i,0} dN_i \geq 0$$

and we get the *Clausius inequality*

$$\boxed{dU - T_0 d\mathcal{S} + P_0 dV - \sum_i \mu_{i,0} dN_i \leq 0. \qquad (3.2)}$$

Here $T_0, P_0, \mu_{i,0}$ are properties of the bath and U, $\mathcal{S}$, V, N_i are properties of the system.

We denote for convenience

$$d\varphi = dU - T_0 d\mathcal{S} + P_0 dV - \sum_i \mu_{i,0} dN_i.$$

Instead of $d\mathcal{S} \geq 0$ we have $d\varphi \leq 0$ for all possible spontaneous processes. In equilibrium no spontaneous process is possible, φ can not decrease and so φ must have a minimum (under the prevailing conditions T_0, P_0, $\mu_{i,0}$). We have a freedom of choosing any function φ that gives the correct differential $d\varphi = dU - T_0 d\mathcal{S} + P_0 dV - \sum_i \mu_{i,0} dN_i$ and a minimum of so-called *free energy* φ gives the equilibrium state.

If the contact with the environment is such that $d\mathcal{S} = dV = dN_i = 0$, Clausius inequality reads $d\varphi = dU \leq 0$, and we can choose $\varphi = U$. In a system with constant entropy, volume and number of particles, energy has its minimum in equilibrium. (How is entropy fixed to a constant value? For the reversible case a constant $\mathcal{S}$ means no heat flow.) Did you ever wonder why the equilibrium state in, for example, mechanics and electrodynamics is that of minimum energy? Here is one answer: second law applied to a system with constant $\mathcal{S}$, V and N_i. For reversible processes with constant $\mathcal{S}$, V, and N_i, $dU = 0$, and thus U is constant.

If the contact keeps V, N_i constant, but allows heat flow to and from the heat bath with temperature T_0, Clausius inequality has the form

$$d\varphi = dU - T_0 d\mathcal{S} \leq 0$$

and we can choose

$$\varphi = U - T_0 \mathcal{S}.$$

Now we check that the differential of φ is correct:

$$d\varphi = dU - T_0 d\mathcal{S} + \mathcal{S} dT_0$$

Temperature is constant, $dT_0 = 0$, and we get

$$d\varphi = dU - T_0 d\mathcal{S},$$

as we wanted. For this system the equilibrium is found by searching for the minimum of Helmholtz free energy F

$$F = U - T_0 \mathcal{S}$$

In a reversible process which keeps $T = T_0, V$ and N_i constant we have $dF = 0$, F is constant, since we are always infinitesimally close to equilibrium.

Table 3.1. Summary of conventional free energy definitions.

constants in a reversible process	freely exchanged quantity	Clausius inequality $d\varphi < 0$	usually chosen φ which has minimum in equilibrium
U, V, N_i		$-T_0 d\mathcal{S} \leq 0 \Rightarrow d\mathcal{S} \geq 0$	$\mathcal{S}$ Entropy (max!)
$\mathcal{S}, V, N_i$		$dU \leq 0$	U Energy
$T = T_0, V, N_i$	heat	$dU - T_0 d\mathcal{S} \leq 0$	$F = U - T_0 \mathcal{S}$ Helmholtz free energy
$P = P_0$, $T = T_0$, N_i	heat, volume	$dU - T_0 d\mathcal{S} + P_0 dV \leq 0$	$G = U - T_0 \mathcal{S} + P_0 V$ Gibbs free energy
$\mathcal{S}, P = P_0, N_i$	volume	$dU + P_0 dV \leq 0$	$H = U + P_0 V$ Enthalpy
$T = T_0$, $\mu_i = \mu_{i,0}$, V	heat, particles	$dU - T_0 d\mathcal{S} - \sum \mu_{i,0} dN_i \leq 0$	$\Omega = U - T_0 \mathcal{S} - \sum \mu_{i,0} N_i$ Grand free energy or grand potential

All the conventional free energies have been collected in Table 3.1. You might wonder what has happened to the surface work terms σdA. We have assumed that system and bath do not exchange surface energy. If there is surface energy it is entirely in the system and included in the system energy U.

NOTE: To keep the extensive variables V, N_i, U, and $\mathcal{S}$ constant we have to build walls that do not move, and do not let particles, energy or heat through. But to keep intensive variables P,μ_i and T constant we have to build walls that move freely or allow free particle or heat exchange with the bath.

Free energies are auxiliary functions of the state of the system *and the environment.* We could always treat the combination of system and environment as an isolated system and find the state that maximises entropy. But it is more straightforward to minimise the appropriate free energy φ.

If a system is connected to a bath with P_0 and/or T_0 and/or $\mu_{i,0}$ constant and we let the situation equilibrate, this means that the internal additional variables like order or distribution of molecules, position of dividing wall or surface settle so that φ has its minimum value. So a given set of constants (P_0 and/or T_0 and/or $\mu_{i,0}$) leads to a unique, well-defined value of free energy φ_{eq}.

Now we study how the equilibrium value of the free energy φ_{eq} changes when we change the bath properties P_0 and/or T_0 and/or $\mu_{i,0}$?

- For a system connected with a heat bath with temperature T_0:
  $\varphi_{\mathrm{eq}} = F_{\mathrm{eq}} = U - T_0\mathcal{S}$, $dF_{\mathrm{eq}} = dU - T_0 d\mathcal{S} - \mathcal{S}dT_0$
  For reversible changes
  $dU = Td\mathcal{S} - PdV + \sum \mu_i dN_i$ and
  $dF_{\mathrm{eq}} = Td\mathcal{S} - PdV + \sum \mu_i dN_i - T_0 d\mathcal{S} - \mathcal{S}dT_0$
  In equilibrium, the temperature is the same as in the bath, $T = T_0$, which leads to
  $dF_{\mathrm{eq}} = -\mathcal{S}dT_0 - PdV + \sum \mu_i dN_i$,
  which shows that
  $$\mu_i = \left(\frac{\partial F_{\mathrm{eq}}}{\partial N_i}\right)_{T,V,N_{i\neq j}} . \tag{3.3}$$
  The Helmholtz free energy F is a suitable thermodynamic potential for systems which interact with the environment only by exchanging heat. For those systems F is constant in equilibrium.
- For a system connected with a temperature and pressure bath with T_0, P_0:
  $\varphi_{\mathrm{eq}} = G_{\mathrm{eq}} = U - T_0\mathcal{S} + P_0 V$, and for reversible changes
  $dG_{\mathrm{eq}} = dU - T_0 d\mathcal{S} - \mathcal{S}dT_0 + P_0 dV + VdP_0$
  In equilibrium, the pressure and temperature are set by the bath, $P = P_0$ and $T = T_0$, which results in
  $\Rightarrow dG_{\mathrm{eq}} = -\mathcal{S}dT_0 + VdP_0 + \sum \mu_i dN_i$,
  $$\mu_i = \left(\frac{\partial G_{\mathrm{eq}}}{\partial N_i}\right)_{T,P,N_{i\neq j}} . \tag{3.4}$$
  The Gibbs free energy G is a wise choice for systems which interact with the environment by exchanging work and heat. For those systems G is constant in equilibrium. In phase transitions both pressure and temperature stay constant, but the order of the system changes. The Gibbs free energy is a suitable potential for studying phase transitions (see p. 127).

- For a system connected with a pressure bath with P_0
  $\varphi_{\mathrm{eq}} = H_{\mathrm{eq}} = U + P_0 V$
  For reversible changes in equilibrium where $P = P_0$
  $dH_{\mathrm{eq}} = -V dP_0 + T d\mathcal{S} + \sum \mu_i dN_i$
  Enthalpy H is the natural choice as a thermodynamic potential for systems which interact with the environment only by exchanging volume work. Enthalpy is also called the heat function or heat content, since enthalpy change for constant pressure processes is equal to the heat exchange. Enthalpy is thus used to define the heat capacity at constant pressure, $C_p = (\partial H/\partial T)_P = (đQ/\partial T)_P$.
- For a system connected with particle and temperature bath with $\mu_{i,0}$, T_0
  $\varphi_{\mathrm{eq}} = \Omega_{\mathrm{eq}} = U - T_0 \mathcal{S} - \sum \mu_{i,0} dN_i$
  For reversible changes in equilibrium $T = T_0, \mu_i = \mu_{i,0}$
  $d\Omega_{\mathrm{eq}} = -\mathcal{S} dT_0 - P dV - \sum N_i d\mu_{i,0}$
  Grand potential Ω is a good thermodynamic potential for systems which interact with the environment by exchanging heat and particles.

These show nicely that

for constant T_0, V, N_i F_{eq} is constant
for constant T_0, P_0, N_i G_{eq} is constant
for constant $P_0, \mathcal{S}, N_i$ H_{eq} is constant
for constant $T_0, V, \mu_{i,0}$ Ω_{eq} is constant

Compare these with Table 3.1 on p. 45.

3.1 Maxwell equations

Take, for example, a system with P, T, N_i constant. Gibbs free energy is the correct thermodynamic potential for the system, and its differential is $dG_{\mathrm{eq}} = -\mathcal{S} dT_0 + V dP_0 + \sum \mu_i dN_i$. We can immediately see that the partial derivatives of the free energy give thermodynamic variables

$$\left(\frac{\partial G_{\mathrm{eq}}}{\partial T_0}\right)_{P_0, N_i} = -\mathcal{S},$$

$$\left(\frac{\partial G_{\mathrm{eq}}}{\partial P_0}\right)_{T_0, N_i} = V,$$

$$\left(\frac{\partial G_{\mathrm{eq}}}{\partial N_i}\right)_{P_0, T_0} = \mu_i$$

and because the second derivative can not depend on the order which the derivatives are taken[1]

---

[1] This is true only for well-defined functions. Not all mathematical entities are so well conditioned.

$$\left(\frac{\partial \mathcal{S}}{\partial P_0}\right)_{T_0,N_i} = -\left(\frac{\partial}{\partial P_0}\left(\frac{\partial G_{\text{eq}}}{\partial T}\right)_{P_0,N_i}\right)_{T,N_i} = \\ -\left(\frac{\partial}{\partial T_0}\left(\frac{\partial G_{\text{eq}}}{\partial P_0}\right)_{T_0,N_i}\right)_{P,N_i} = -\left(\frac{\partial V}{\partial T_0}\right)_{P_0,N_i} .$$

Similarly from second derivatives we get

$$\left(\frac{\partial V}{\partial N_i}\right)_{T_0,P_0,N_{j\neq i}} = \left(\frac{\partial \mu_i}{\partial P_0}\right)_{T_0,N_i} \tag{3.5}$$

and

$$\left(\frac{\partial \mathcal{S}}{\partial N_i}\right)_{T_0,P_0,N_{j\neq i}} = \left(\frac{\partial \mu_i}{\partial T_0}\right)_{P_0,N_i} .$$

According to the definition of partial molecular volume (eq. 2.11) we have $\left(\frac{\partial V}{\partial N_i}\right)_{T_0,P_0,N_{j\neq i}} \equiv v_i$, and Maxwell equation (3.5) takes the familiar form

$$v_i = \left(\frac{\partial \mu_i}{\partial P_0}\right)_{T_0,x_i} ,$$

which we have already used.

NOTE: Since chemical potential as an intensive quantity depends only on the composition of the system, not the size of it, we can replace constant N_i with constant x_i.

Other free energies U, H, F and Ω can be used to derive more Maxwell equations:

Internal energy U

$$\left(\frac{\partial T}{\partial V}\right)_{\mathcal{S},N_i} = -\left(\frac{\partial P}{\partial \mathcal{S}}\right)_{V,N_i} \qquad \left(\frac{\partial T}{\partial N_i}\right)_{\mathcal{S},V,N_{j\neq i}} = \left(\frac{\partial \mu_i}{\partial \mathcal{S}}\right)_{V,N_i}$$

$$\left(\frac{\partial P}{\partial N_i}\right)_{\mathcal{S},V,N_{j\neq i}} = -\left(\frac{\partial \mu_i}{\partial V}\right)_{\mathcal{S},N_i}$$

Enthalpy H

$$\left(\frac{\partial T}{\partial P}\right)_{\mathcal{S},N_i} = \left(\frac{\partial V}{\partial \mathcal{S}}\right)_{P,N_i} \qquad \left(\frac{\partial T}{\partial N_i}\right)_{\mathcal{S},P,N_{j\neq i}} = \left(\frac{\partial \mu_i}{\partial \mathcal{S}}\right)_{P,N_i}$$

$$\left(\frac{\partial V}{\partial N_i}\right)_{\mathcal{S},P,N_{j\neq i}} = \left(\frac{\partial \mu_i}{\partial P}\right)_{\mathcal{S},N_i}$$

Helmholtz free energy F

$\left(\frac{\partial \mathcal{S}}{\partial V}\right)_{T,N_i} = \left(\frac{\partial P}{\partial T}\right)_{V,N_i}$ $\left(\frac{\partial P}{\partial N_i}\right)_{T,V,N_{j\neq i}} = -\left(\frac{\partial \mu_i}{\partial V}\right)_{T,N_i}$

$\left(\frac{\partial P}{\partial N_i}\right)_{T,V,N_{j\neq i}} = -\left(\frac{\partial \mu_i}{\partial V}\right)_{T,N_i}$

Grand potential Ω

$\left(\frac{\partial \mathcal{S}}{\partial V}\right)_{T,\mu_i} = \left(\frac{\partial P}{\partial T}\right)_{V,\mu_i}$ $\left(\frac{\partial \mathcal{S}}{\partial \mu_i}\right)_{T,V,\mu_{j\neq i}} = \left(\frac{\partial N_i}{\partial T}\right)_{V,\mu_i}$

$\left(\frac{\partial P}{\partial \mu_i}\right)_{T,V} = \left(\frac{\partial N_i}{\partial v}\right)_{T,\mu_i}$

Gibbs free energy G (also here for completeness)

$\left(\frac{\partial V}{\partial N_i}\right)_{T,P,N_{j\neq i}} = \left(\frac{\partial \mu_i}{\partial P}\right)_{T,N_i}$ $\left(\frac{\partial \mathcal{S}}{\partial N_i}\right)_{T,P,N_{j\neq i}} = \left(\frac{\partial \mu_i}{\partial T}\right)_{P,N_i}$

$\left(\frac{\partial \mathcal{S}}{\partial P}\right)_{T,N_i} = -\left(\frac{\partial V}{\partial T}\right)_{P,N_i}$

3.2 Free energy. Free for what?

The free energies φ are also called thermodynamic potentials: the potential has a minimum in the equilibrium. Now we start to see that it is probably a free energy barrier that the system tries to overcome in phase transitions, but gets trapped to the "wrong" side of the mountain as in Fig. 2.16.

Let us think of a system connected with a pressure bath with pressure P_0, so that the volume of the system can change, but heat does not flow in or out. Initially the energy of the system is U_0. If we somehow took energy $\Delta E (> 0)$ from the system and if the system was otherwise isolated, the final energy would be $U_0 - \Delta E$. But now the pressure is kept constant, which results in an energy change $-P_0 \Delta V$ between the system and the bath since system volume changes. The actual final energy of the system is

$$U = U_0 - \Delta E - P_0 \Delta V,$$

and the energy change is

$$\Delta U = U - U_0 = -\Delta E - P_0 \Delta V,$$

and the energy taken from the system is

$$\Delta E = -(\Delta U + P_0 \Delta V) = -\Delta H = -\Delta \varphi.$$

So the amount of energy that is available to be taken out of the "system" is not the internal energy of the system U, but $H = U + P_0 V$ due to the connection with the bath. In reality the energy comes both from the system and the bath. Similar reasoning can be applied to other thermodynamic potentials.

3.3 Free energy diagrams

The free energy φ of the system is a function of the order parameter x (for example density). In the following we think of homogeneous systems, where x is the same in the whole system (the whole system is vapour or liquid, only one phase, no droplets). Fig. 3.3 shows schematic free energy curves in a one-component system as functions of density with different saturation ratios S.

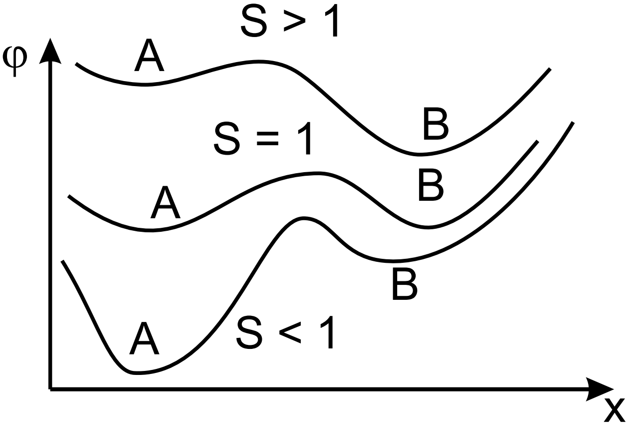


Fig. 3.3. Free energy curves as functions of density x with different saturation ratios S.

If x is the density of the fluid, minimum A corresponds to vapour (lower ρ). It is the true global equilibrium state for $S < 1$. Minimum B corresponds to liquid (higher ρ). It is the true equilibrium when $S > 1$. But it can be seen that the system can be trapped behind a barrier.

If we plot the free energies corresponding to the minima in Fig. 3.3 as functions of saturation ratio, we obtain Fig. 3.4, where A is the equilibrium free energy curve with vapour density, B with liquid density. Phase change should happen at $S = 1$ because nature should settle to the global minimum of free energy. Saturation ratio $S > 1$ drives the phase transition from vapour to liquid.

NOTE: Instead of temperature T or vapour pressure P as such, the combination of them in the form of saturation ratio $S = \frac{P}{P_e(T)}$ is the key quantity telling us which phase is stable in the prevailing conditions.

3.4 Free energy change in droplet formation

Now we return to the case of a spherical cluster forming in a vapour phase. We study the free energy change in a process where the initial state (referred

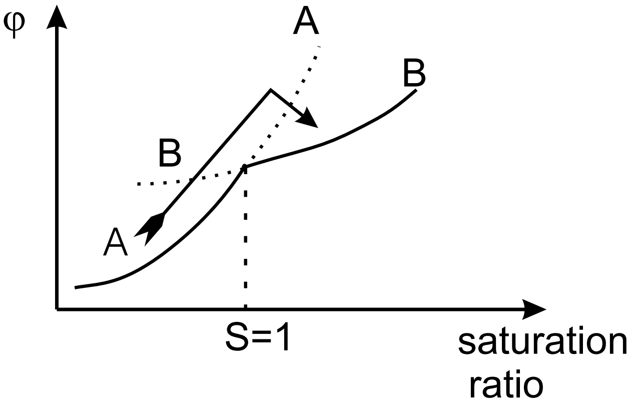


Fig. 3.4. Free energy in the equilibrium system as a function of saturation ratio S. The points forming the curves correspond to the location of the minima A and B in Fig. 3.3. The arrow shows the route taken by a vapour when saturation is exceeded, it follows the metastable part of curve A until disturbance, nucleation or reaching the spinodal pressure drops the system to curve B, which is the stable state when $S > 1$.

to by subscript 0) is a homogeneous vapour, and the final state is a cluster surrounded by the vapour. The temperature of the system is from now on assumed to be constant and equal to that of the heat bath T_0.

In general, the energy of a homogeneous part of the system has the form

$$U = T_0\mathcal{S} - PV + \sigma A + \sum \mu_i N_i.$$

The total energy of the system is a sum of the energies of the surface (no volume $V = 0$), and bulk vapour and liquid (no surface area $A = 0$) contributions. The initial energy of the homogeneous vapour is

$$U_0 = T_0\mathcal{S}_0 - P_0V_0 + \sum \mu_{i,g}^0 N_{i,g}^0.$$

The final energy in the system consisting of the cluster surrounded by vapour is then

$$U = T_0\mathcal{S} - P_gV_g - P_lV_l + \sigma A + \sum \mu_{i,g}N_{i,g} + \sum \mu_{i,l}N_{i,l} + \sum \mu_{i,s}N_{i,s}.$$

In the case of a droplet forming in a vapour there are at least three choices for the free energy. The choice depends on the conditions of the real nucleation event (in nature or laboratory) or hypothetical mind experiment. The suitable free energy is different depending on which quantities are held constant when the droplet forms.

1. The chemical potentials in the gas phase $\mu_{i,g} = \mu_{i,g}^0$ and total volume $V_0 = V_g + V_l$ are kept constant.

The grand free energy in the initial state is

$$\Omega_0 = U_0 - T_0\mathcal{S}_0 - \sum \mu_{i,g}^0 N_{i,g}^0 = -P_0V_0 = -P_0(V_l + V_g)$$

and in the final state

$$\begin{aligned}\Omega = U - T_0\mathcal{S} - \sum \mu_{i,g}^0 N_{i,\mathrm{tot}} &= U - T_0\mathcal{S} - \sum \mu_{i,g}^0 (N_{i,g} + N_{i,l} + N_{i,s}) \\ &= -P_gV_g - P_lV_l + \sigma A + \sum(\mu_{i,l} - \mu_{i,g}^0)N_{i,l} + \sum(\mu_{i,s} - \mu_{i,g}^0)N_{i,s}.\end{aligned}$$

The grand free energy change in the droplet formation is then

$$\begin{aligned}\Delta\Omega =& (P_0 - P_l)V_l + (P_0 - P_g)V_g + \sigma A \\ & + \sum(\mu_{i,l} - \mu_{i,g}^0)N_{i,l} + \sum(\mu_{i,s} - \mu_{i,g}^0)N_{i,s}.\end{aligned}$$

Now if we assume that besides the chemical potentials $\mu_{i,g}$, the composition of the gas stays constant, also the pressure must be unchanged according to the Maxwell equation (2.13), which gives

$$0 = d\mu_{i,g}\Big|_{x_{i,g},T} = v_{i,g}dP_g \Rightarrow dP_g = 0 \Rightarrow P_g = P_0$$

and we get for the formation free energy

$$\boxed{\Delta\Omega = (P_0 - P_l)V_l + \sigma A + \sum(\mu_{i,l} - \mu_{i,g}^0)N_{i,l} + \sum(\mu_{i,s} - \mu_{i,g}^0)N_{i,s}. \quad (3.6)}$$

2. The pressure of the gas is constant $P_g = P_0$, and the total molecular numbers are unchanged $N_{i,\mathrm{tot}} = N_{i,l} + N_{i,g} + N_{i,s} = N_{i,g}^0$.
   Then the Gibbs free energies in the initial and final states are

$$G_0 = U_0 - T_0\mathcal{S}_0 + P_0V_0 = \sum \mu_{i,g}^0 N_{i,g}^0 \qquad (3.7)$$

$$\begin{aligned}G &= U - T_0\mathcal{S} + P_0V_{\mathrm{tot}} = U - T_0\mathcal{S} + P_0(V_g + V_l) \qquad (3.8) \\ &= (P_0 - P_l)V_l + \sigma A + \sum \mu_{i,g}N_{i,g} + \sum \mu_{i,l}N_{i,l} + \sum \mu_{i,s}N_{i,s}.\end{aligned}$$

The Gibbs free energy change in the droplet formation is

$$\begin{aligned}\Delta G =& (P_0 - P_l)V_l + \sigma A \\ & + \sum \mu_{i,g}N_{i,g} + \sum \mu_{i,l}N_{i,l} + \sum \mu_{i,s}N_{i,s} - \sum \mu_{i,g}^0 N_{i,g}^0.\end{aligned}$$

Furthermore, assuming that composition of the gas phase is unchanged which due to constant pressure and the Maxwell equation (2.13) means also that the chemical potential is constant $\mu_{i,g} = \mu_{i,g}^0$, and using the fact that

$$N_{i,\mathrm{tot}} = N_{i,l} + N_{i,g} + N_{i,s} = N_{i,g}^0$$

we get

$$\begin{aligned}\Delta G &= (P_0 - P_l)V_l + \sigma A + \sum \mu_{i,g}^0 (N_{i,g} - N_{i,g}^0) + \sum \mu_{i,l} N_{i,l} + \sum \mu_{i,s} N_{i,s} \\ &= (P_0 - P_l)V_l + \sigma A + \sum \mu_{i,g}^0 (-N_{i,l} - N_{i,s}) + \sum \mu_{i,l} N_{i,l} + \sum \mu_{i,s} N_{i,s} \\ &= (P_0 - P_l)V_l + \sigma A + \sum (\mu_{i,l} - \mu_{i,g}^0) N_{i,l} + \sum (\mu_{i,s} - \mu_{i,g}^0) N_{i,s}.\end{aligned}$$

3. The total molecular numbers are constant $N_{i,\mathrm{tot}} = N_{i,l} + N_{i,g} + N_{i,s} = N_{i,g}^0$ and the volume of the system $V_{\mathrm{tot}} = V_g + V_l$ does not change.
   Then the Helmholtz free energies in the initial and final states read

$$\begin{aligned}F_0 =& U_0 - T_0 \mathcal{S}_0 = -P_0(V_l + V_g) + \sum \mu_{i,g}^0 N_{i,g}^0 \\ F =& U - T_0 \mathcal{S} = -P_g V_g - P_l V_l + \sigma A \\ &+ \sum \mu_{i,l} N_{i,l} + \sum \mu_{i,g} N_{i,g} + \sum \mu_{i,s} N_{i,s}.\end{aligned}$$

The change in the Helmholtz free energy is

$$\begin{aligned}\Delta F =& (P_0 - P_l)V_l + (P_0 - P_g)V_g + \sigma A \\ &+ \sum (\mu_{i,g} - \mu_{i,g}^0) N_{i,g} + \sum (\mu_{i,l} - \mu_{i,g}^0) N_{i,l} + \sum (\mu_{i,s} - \mu_{i,g}^0) N_{i,s}.\end{aligned}$$

Assuming that droplet formation does not affect the gas pressure $P_0 = P_g$ and composition means (again due to Maxwell equation 2.13) unchanged chemical potentials, $\mu_{i,g} = \mu_{i,g}^0$, we get

$$\Delta F = (P_0 - P_l)V_l + \sigma A + \sum (\mu_{i,l} - \mu_{i,g}^0) N_{i,l} + \sum (\mu_{i,s} - \mu_{i,g}^0) N_{i,s}.$$

NOTE: Only the gas phase is connected to the heat/particle/pressure bath. So the free energy of the whole system can not be calculated as a sum of free energies of gas, liquid and surface:

$$\begin{aligned}\Omega &\neq \Omega_l + \Omega_g + \Omega_s \\ G &\neq G_l + G_g + G_s \\ F &\neq F_l + F_g + F_s\end{aligned}$$

$\Omega_l, \Omega_g, \Omega_s$ *and so on would be the free energies of liquid, gas and surface if each of these phases were directly connected to the baths. But now only the gas phase is connected to the bath, which is the basis or definition of free energies, and thus free energies for liquid and surface phases are not well defined. But energy is always the sum of liquid, gas and surface contributions*

$$U = U_l + U_g + U_s$$

and we have started all our derivations from this.

With the assumptions we made, the change in the free energy is always the same $\Delta\Omega = \Delta G = \Delta F$. All the assumptions are essentially the same: the gas tank is large and the cluster is small, so that its formation does not change the state of the vapour significantly. Equilibrium is found by setting the derivatives of $\Delta\Omega, \Delta G$ or ΔF to zero. We get equilibrium conditions by keeping the pressure P_0 and chemical potential $\mu_{i,g}^0$ constant, and taking the derivatives with respect to

- V, keeping $N_{i,l}$ and $N_{i,s}$ constant,
- $N_{i,l}$, keeping $N_{j,l}, j \neq i$ and $N_{i,s} \forall i$ constant,
- $N_{i,s}$, keeping $N_{j,s}, j \neq i$ and $N_{i,l} \forall i$ constant,

and setting these derivatives equal to zero. Equilibrium is from now on denoted by * and occurs of course when the equilibrium conditions (2.7) and (2.8) are satisfied:

$$P_l^* - P_0 = \frac{2\sigma^*}{r^*},$$

$$\mu_{i,l}^* = \mu_{i,g}^* = \mu_{i,s}^*.$$

To get these familiar conditions from derivatives of $\Delta\Omega, \Delta G$ or ΔF [2] you have to use the Gibbs-Duhem equation (1.9) in the isothermal case $dT = 0$ for bulk gas and liquid (p. 12)

$$V_g dP_g = \sum N_{i,g} d\mu_{i,g},$$

$$V_l dP_l = \sum N_{i,l} d\mu_{i,l}$$

and the Gibbs adsorption isotherm (1.12) for the surface contribution

$$-A d\sigma = \sum N_{i,s} d\mu_{i,s}.$$

For the equilibrium cluster, also known as a *critical cluster*, we can use the equality of chemical potentials and then the Laplace equation (2.8), and finally the expressions of volume and surface area of a spherical cluster in terms of its radius r^* to simplify the formula for the formation free energy (any of $\Delta\Omega$, ΔF or ΔG, denoted generally $\Delta\varphi$)

$$\Delta\varphi^* = (P_0 - P_l^*)V_l^* + \sigma A = \frac{-2\sigma^*}{r^*} V_l^* + \sigma^* A^* = \frac{-2\sigma^*}{r^*} \frac{4}{3}\pi r^{*3} + \sigma^* 4\pi r^{*2}$$

which leads to a compact form for the formation energy of the critical cluster

---

[2] *NOTE: you really should take the derivative of the final state free energies Ω, G or F, but initial state free energies Ω_0, G_0, F_0 are constants, so $d\Delta\Omega = d\Omega - d\Omega_0 = d\Omega$ and so on.*

$$\boxed{\Delta\varphi^* = \frac{4}{3}\pi\sigma^* r^{*2},} \tag{3.9}$$

which is easy to remember as one third of the surface energy of the cluster.

3.5 Classical droplet model

The density profiles and molecular positions in a real cluster with two components are sketched in Fig. 3.5. In this example component 2 is *surface active.* It accumulates near the droplet surface.

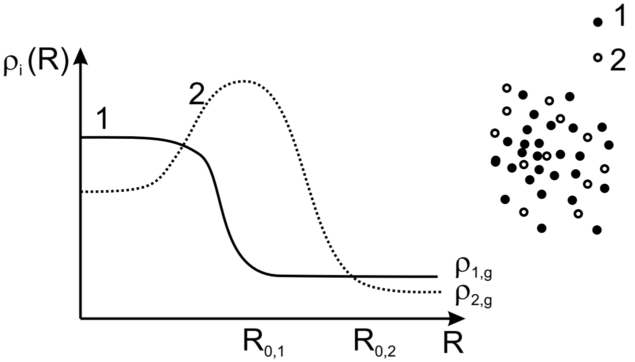


Fig. 3.5. Molecular densities of components 1 and 2 as functions of distance from the centre of a real spherical droplet and a picture of the molecular positions in the droplet (cluster). $\rho_{1,g}$ and $\rho_{2,g}$ are the densities of the two components in the vapour far from the droplet. $R_{0,i}$ is the distance where the density of component i has reached the vapour phase value.

The classical spherical droplet model simplifies the situation as shown in Fig. 3.6.

We can choose the dividing surface radius r arbitrarily. The liquid inside the sphere is considered a macroscopic hypothetical bulk liquid. The bulk density is given by experimental formula for the total density of molecules in the liquid $\rho_l(x_{i,l}, T) = \sum_i \rho_{i,l}$, which we simply call the liquid density. In homogeneous bulk liquid the densities of individual components are given by

$$\rho_{i,l} = x_{i,l}\rho_l(x_{i,l}, T).$$

For an equilibrium droplet the bulk liquid mole fractions $x^*_{i,l}$ are solved from equations (2.23)

$$\frac{\Delta\mu_i}{v_{i,l}} = \frac{\Delta\mu_1}{v_{1,l}} \tag{3.10}$$

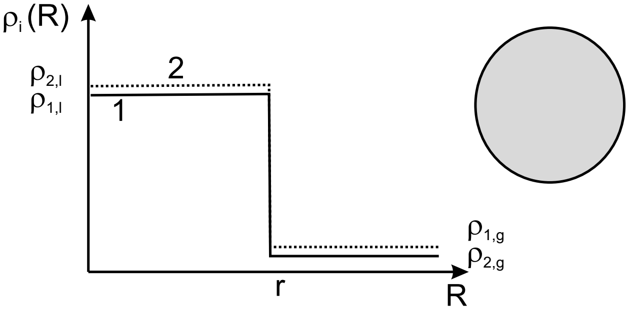


Fig. 3.6. Simplified molecular densities of components 1 and 2 as functions of distance from the centre of a droplet and the cluster model in the classical droplet model. $\rho_{1,g}$ and $\rho_{2,g}$ are the densities of the two components in the vapour far from the droplet. $\rho_{1,l}$ and $\rho_{2,l}$ are the densities of the two components in the bulk liquid. r is the position of the dividing surface.

when we know the vapour densities (pressures) of all the components i. The number of molecules in our model droplet are given by

$$N_{i,l} = \frac{4}{3}\pi r^3 \rho_{i,l} = \frac{4}{3}\pi r^3 x_{i,l}\rho_l(x_{i,l}, T).$$

Partial molecular volumes $v_{i,l}$ are calculated from bulk liquid density ρ_l, so they are bulk partial molecular volumes. (They tell us how much the volume changes when you add one molecule to a large pool of liquid, not to the cluster.)

NOTE: From now on subscript d stands for droplet, meaning the sum of bulk liquid and surface phase contributions. Subscript tot most often refers to the whole system, in other words sum of gas, surface and liquid phase contributions. $N_{i,l}$ *are often called numbers of molecules in the core of the cluster, while* $N_{i,d} = N_{i,l} + N_{i,s}$ *are the total numbers of molecules in the cluster.*

In the real cluster/droplet the total number of molecules is an integral of the density profile

$$N_{i,d} = \int_0^{R_{i,o}} \rho_i(R) 4\pi R^2 dR$$

where $R_{i,o}$ is a point where the position dependent the density $\rho_i(r)$ has lowered to the vapour level $\rho_i(R_{i,o}) = \rho_{i,g}$. The *surface excess* numbers $N_{i,s}$ are introduced as correction terms to the core numbers

$$N_{i,s} = N_{i,d} - N_{i,l}$$

and thus

$$N_{i,d} = N_{i,l} + N_{i,s}.$$

For the equilibrium droplet component densities $\rho_{i,l}$ are set by the equilibrium conditions (eq. 3.10), and do not depend on the choice of the dividing surface.

This means that the core $N_{i,l}$ and surface numbers $N_{i,s}$ are dependent on the choice of the positions of the surface, but the total numbers of molecules in the cluster/droplet $N_{i,d} = N_{i,l} + N_{i,s}$ are independent of it.

NOTE: The liquid mole fraction can not be calculated from the total numbers of molecules on the cluster $N_{i,d}$

$$x_{i,l} = \frac{N_{i,l}}{\sum N_{k,l}} \neq \frac{N_{i,d}}{\sum N_{k,d}} = \frac{N_{i,l} + N_{i,s}}{\sum (N_{k,l} + N_{k,s})},$$

so if we know that a cluster has in total 7 water molecules and 4 sulphuric acid molecules, we do not directly know the composition of the hypothetical bulk liquid

$$x_{2,l} \neq \frac{4}{11} = \frac{N_{2,d}}{N_{1,d} + N_{2,d}}.$$

3.6 Surface of tension

We have actually already made a hidden assumption on the position of the dividing surface (Abraham 1974). Let's look at the energy of an *equilibrium* droplet in vapour with pressure P_g^0 and chemical potential $\mu_{i,g}$. The energy of the system is

$$U^* = T_0 \mathcal{S}_{\text{tot}}^* - P_l^* V_l^* - P_g^0 V_g^* + \sigma^* A^* + \sum \mu_{i,l}^* N_{i,l}^* + \sum \mu_{i,s}^* N_{i,s}^* + \sum \mu_{i,g}^0 N_{i,g}^*.$$

For equilibrium, chemical potentials in all the phases are the same

$$\mu_{i,l}^* = \mu_{i,s}^* = \mu_{i,g}^0$$

and the droplet energy takes the form

$$\begin{aligned} U^* &= T_0 \mathcal{S}_{\text{tot}}^* - P_l^* V_l^* - P_g^0 V_g^* + \sigma^* A^* + \sum \mu_{i,g}^0 (N_{i,l}^* + N_{i,s}^* + N_{i,g}^*) \\ &= T_0 \mathcal{S}_{\text{tot}}^* - P_l^* V_l^* - P_g^0 V_g^* + \sigma^* A^* + \sum \mu_{i,g}^0 N_{i,\text{tot}}. \end{aligned} \tag{3.11}$$

If we now move the dividing surface, but keep the physical situation unchanged U^*, T_0, S_{tot}^*, $\mu_{i,g}^0$, $N_{i,\text{tot}}^*$, P_g and $V_{\text{tot}} = V_l^* + V_g^*$ must stay constant, and also $x_{i,l}^*$ defined by equilibrium conditions (3.10) is constant. The Maxwell equation (2.13) gives the result

$$dP_l^* = \frac{1}{v_{i,l}} d\mu_{i,l}^* = \frac{1}{v_{i,l}} d\mu_{i,g}^0 = 0,$$

and thus also P_l^* is constant.

By square brackets we denote the derivative associated with the displacement of the dividing surface keeping the real physical system unchanged. Volume, area and radius are connected through equations $V^* = \frac{4}{3}\pi r^{*3}$, $A^* = 4\pi r^{*2}$, $\frac{dA^*}{dr^*} = 8\pi r^*$, and $\frac{dV^*}{dr^*} = 4\pi r^{*2} = A^*$. Taking the derivative of the energy in eq. (3.11) we get

$$0 = \left[\frac{dU^*}{dV_l^*}\right] = -P_l^* - P_g^0 \left[\frac{dV_g^*}{dV_l^*}\right] + \left[\frac{d\sigma^*}{dV^*}\right] A^* + \sigma^* \left[\frac{dA^*}{dV^*}\right]$$

and using

$$\left[\frac{dV_g^*}{dV_l^*}\right] = -1$$

together with

$$\frac{dA^*}{dV^*} = \frac{dA^*}{dr^*} \cdot \frac{1}{\left(\frac{dV^*}{dr^*}\right)} = \frac{8\pi r^*}{4\pi r^{*2}} = \frac{2}{r^*}$$

we obtain an equation

$$0 = -P_l^* + P_g^0 + \frac{2\sigma^*}{r^*} + \left[\frac{d\sigma^*}{dr^*}\right] \cdot \frac{1}{\frac{dV^*}{dr^*}} A^*$$

which leads to the *generalised Laplace equation*

$$\boxed{P_l^* - P_g^0 = \frac{2\sigma^*}{r^*} + \left[\frac{d\sigma^*}{dr^*}\right]. \qquad (3.12)}$$

To get the usual Laplace equation (2.8) we have to choose the dividing surface so that

$$\left[\frac{d\sigma^*}{dr^*}\right] = 0.$$

This choice is called the *surface of tension.* If we have chosen the surface of tension our system satisfies the Gibbs adsorption isotherm (1.12)

$$Ad\sigma = -\sum N_{i,s} d\mu_{i,s}$$

and the first law in the form

$$dU = TdS - PdV + Ad\sigma + \sum \mu_i dN_i S$$

but these basic equations are not valid with some arbitrary choice of dividing surface. Also the thermodynamic surface tension is equal to the mechanical surface tension (p. 8) only if we calculate the former at the surface of tension. There is no concrete physical meaning for the surface of tension: it is the mathematical choice for the dividing surface that we have to make to be able to link the surface tension to its experimentally measurable values.

Notice that the Laplace equation (2.8) can be derived in many ways, and we have gone through three of them.

1. On p. 21 it was derived by requiring that entropy has a maximum with respect to all variables, in particular to the volume change of the droplet.
2. On p. 54 it was explained how the Laplace equation can be derived by finding the extremum of the free energy with respect to all variables, in particular droplet volume, which is actually just another way of maximising entropy. Remember that free energies are derived to make it easy to maximise entropy in a system connected with the environment.
3. Now we derived the Laplace equation from the fact that the energy of the system can not be affected by the mathematical choice of the dividing surface, a choice which has no physical significance.

3.7 Equimolar surface and size dependence of surface tension

The only surface tension we normally know is the one measured for a flat surface. Surface tension can be very different for small, highly curved droplets. Now we derive a condition of curvature independence of surface tension using the Gibbs adsorption isotherm (1.12)

$$Ad\sigma = -\sum_i N_{i,s} d\mu_{i,s}.$$

We study an equilibrium droplet for which the chemical potentials and pressure satisfy

$$d\mu_{i,s}^* = d\mu_{i,l}^* = v_{i,l}^* dP_l^*$$

if the composition $x_{i,l}^*$ is kept constant (Maxwell 2.13). We change the gas phase partial vapour pressures so that $x_{i,l}^*$ stays unchanged, but the size of the equilibrium droplet grows

$$A\left(\frac{d\sigma^*}{dr^*}\right) = -\sum N_{i,s} v_{i,l} \left(\frac{dP_l^*}{dr^*}\right) = -\left(\frac{dP_l^*}{dr^*}\right) \sum N_{i,s} v_{i,l}.$$

Now it is evident that if we want the surface tension to be independent of the curvature (size of the droplet when composition is constant) we have to choose the dividing surface so that

$$\sum N_{i,s} v_{i,l} = 0. \tag{3.13}$$

This surface is called the *equimolar surface*, because for one-component systems it means that $N_s = 0$ and the total number of molecules in the droplet N_d is the same as the number of molecules in bulk liquid N_l since now $N_d = N_l + 0$. The choice of equimolar surface is illustrated in Fig. 3.7.

For multicomponent systems it is impossible to choose a surface for which $N_{i,s} = 0$ for all components i at the same time, but it is possible to satisfy eq.

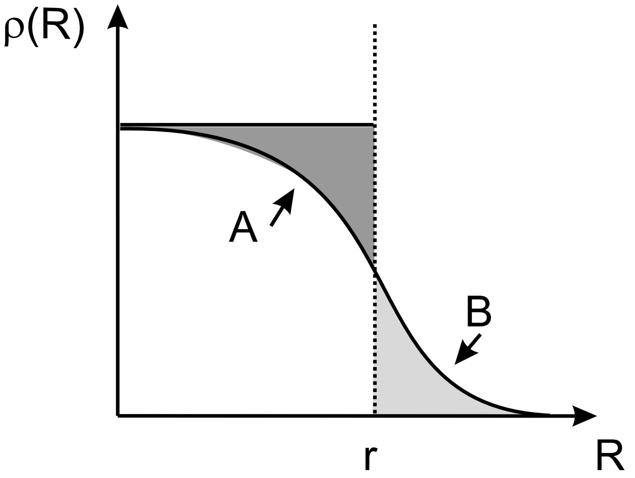


Fig. 3.7. Density as a function of the distance from the centre of a spherical cluster in one-component system. The dashed line illustrates the position of the equimolar surface for which areas A and B are equal.

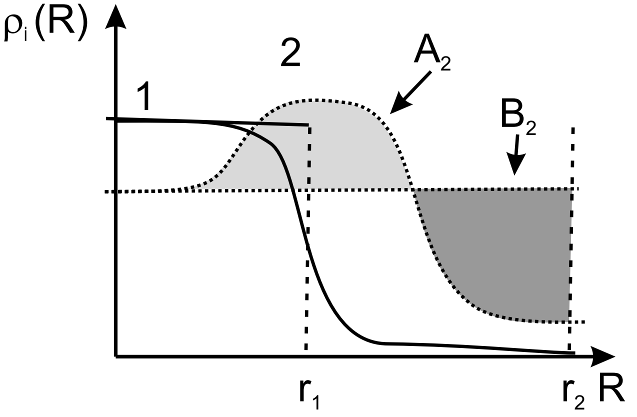


Fig. 3.8. Densities of components 1 and 2 as a function of the distance from the centre of a spherical cluster in a two-component system. Radius r_2 illustrates the position of the equimolar surface for component 2 for which areas A_2 and B_2 are equal, and r_1 is the equimolar surface for component 1. For clarity areas A_1 and B_1 are not marked in this Figure, but they can be seen in Fig. 3.7.

(3.13). If the partial molecular volumes are positive (as they usually, but not necessarily are) for all components i in a multicomponent case condition (3.13) lead to negative surface numbers for at least one of the components $N_{i,s} < 0$. Remember that the surface excess numbers are correction terms, not real numbers of molecules in a certain volume, so the fact that they can be negative is not unphysical. The theory is based on the idea that surface excess numbers are small corrections to the core numbers. If they are comparable in size the theory is most likely applied to a system where its validity is questionable. Large negative surface excess can lead to negative total number of molecules, which is a unphysical result and will be discussed further on p. 124.

For equimolar surface the volume of the cluster can be calculated either based on total numbers in the cluster $N_{i,d}$ or numbers in the bulk liquid $N_{i,l}$, as we see with the help of eq. (2.12) ($V = \sum N_i v_{i,l}$, see p. 28)

$$\begin{aligned}\frac{4}{3}\pi r^3 = V_l = \sum_i N_{i,l}v_{i,l} = \sum_i N_{i,l}v_{i,l} + 0 = \sum_i N_{i,l}v_{i,l} + \sum_i N_{i,s}v_{i,l} \\ = \sum_i (N_{i,l} + N_{i,s})v_{i,l} = \sum_i N_{i,d}v_{i,l}.\end{aligned} \tag{3.14}$$

NOTE: Since we know the surface tension only for the surface of tension and flat surface, we have to hope that surface of tension coincides with the equimolar surface, and proceed as if this were the case. This is a crucially false assumption for surface active systems, where one of the components concentrates on the surface. Using surface tension of planar surface for curved surfaces is called the **capillary approximation**.

3.8 Conventional form of droplet formation free energy

Now we transform the free energy change in droplet formation given for example by eq. (3.6)

$$\Delta\varphi = (P_0 - P_l)V_l + \sigma A + \sum(\mu_{i,l} - \mu_{i,g}^0)N_{i,l} + \sum(\mu_{i,s} - \mu_{i,g}^0)N_{i,s}$$

into a more practical form. P_0 is the pressure of the gas phase and the Maxwell equation (2.13) tells that $d\mu_{i,l} = V_{i,l}dP_l$ when the composition is constant. This Maxwell equation can be integrated for an incompressible liquid to get

$$\mu_{i,l}(P_l) - \mu_{i,l}(P_0) = v_{i,l}(P_l - P_0)$$

and when we multiply this by $N_{i,l}$ and sum over all components i and use result (3.14) we get

$$\begin{aligned}\sum \left[\mu_{i,l}(P_l) - \mu_{i,l}(P_0)\right]N_{i,l} =& \sum N_{i,l}v_{i,l}(P_l - P_0) \\ =& (P_l - P_0)\sum N_{i,l}v_{i,l} = (P_l - P_0)V_l\end{aligned}$$

which means

$$(P_0 - P_l)V_l = -\sum \left[\mu_{i,l}(P_l) - \mu_{i,l}(P_0)\right]N_{i,l}.$$

Now we substitute this to $\Delta\varphi$ and get

$$\begin{aligned}\Delta\varphi = & -\sum \big[\mu_{i,l}(P_l) - \mu_{i,l}(P_0)\big] N_{i,l} + \sigma A \\ & + \sum (\mu_{i,l} - \mu^0_{i,g}) N_{i,l} + \sum (\mu_{i,s} - \mu^0_{i,g}) N_{i,s}\end{aligned}$$

The terms with $\mu_{i,l}(P_l) \equiv \mu_{i,l}$ cancel and using the definition of $\Delta\mu$ (eq. 2.14) we get

$$\begin{aligned}\Delta\varphi &= \sum (\mu^0_{i,g} - \mu_{i,l}(P_0)) N_{i,l} + \sigma A + \sum (\mu_{i,s}(P_0) - \mu^0_{i,g}) N_{i,s} \\ &= \sum \Delta\mu_{i,l} N_{i,l} + \sigma A + \sum (\mu_{i,s} - \mu^0_{i,g}) N_{i,s} \qquad (3.15)\end{aligned}$$

Kelvin equations can be obtained by taking the derivative of (3.15) with respect to bulk and surface excess molecular numbers one at a time. The Gibbs-Duhem equation and the Gibbs adsorption isotherm must be used in the process.

For the equilibrium cluster, chemical potentials in all phases are equal, $\mu^*_{i,s} = \mu^0_{i,g}$. The formation free energy can be written as

$$\Delta\varphi^* = \sum \Delta\mu^*_{i,l} N^*_{i,l} + \sigma^* A^*$$

and we do not have to worry about the surface excess molecules, but if we want to plot $\Delta\varphi$ as a function of numbers of molecules $N_{i,d}$ (or $N_{i,l}$) and find the equilibrium point from the figure, we need to know $\Delta\varphi$ also for non-equilibrium clusters.

3.9 One-component case

If we choose the equimolar surface as the dividing surface, which means $N_{i,s} = 0$ and $N_d = N_l$, and we also assume that the vapour behaves like an ideal gas (eq. (2.20) for one component case) we have $\Delta\mu = -kT_0 \ln S$ and the formation free energy of eq. (3.15) becomes

$$\Delta\varphi = \Delta\mu N_d + \sigma A = -N_d k T_0 \ln S + \sigma A.$$

Now we express the area in terms of the molecular number using $V = N_d v_l = \frac{4}{3}\pi r^3$, $r = \big(\frac{3V}{4\pi}\big)^{1/3}$ and

$$A = 4\pi r^2 = 4\pi \Big(\frac{3V}{4\pi}\Big)^{2/3} = \Big(\frac{4^3\pi^3 3^2}{4^2\pi^2}\Big)^{1/3} v_l^{2/3} N_d^{2/3} = \big(36\pi\big)^{1/3} v_l^{2/3} N_d^{2/3}.$$

Inserting this to the expression of the formation free energy gives

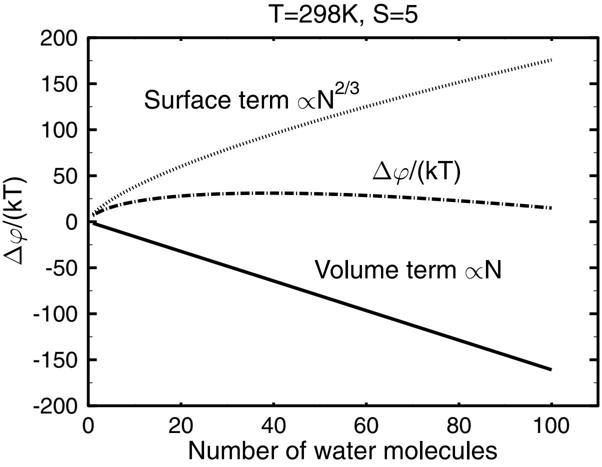


Fig. 3.9. Droplet formation free energy as a function of the number of molecules in the droplet for pure water. The surface and volume contributions to the free energy are shown separately. The volume term is a straight line with a slope $\Delta\mu = -kT \ln S$, and the slope of the surface term depends both on liquid density (molecular volume) and surface tension.

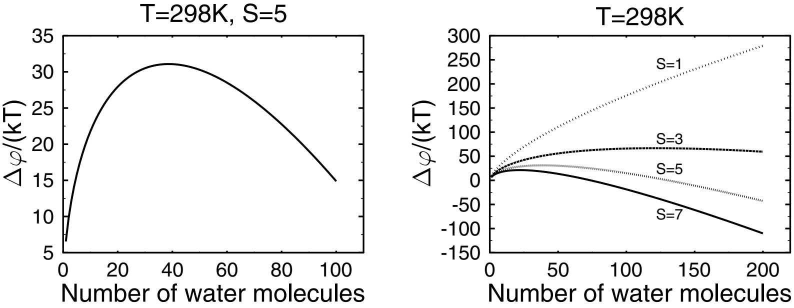


Fig. 3.10. Droplet formation free energy as a function of the number of molecules in the droplet for pure water with different saturation ratios S.

$$\boxed{\Delta\varphi = -N_d k T_0 \ln S + N_d^{2/3} \sigma (36\pi)^{1/3} v_l^{2/3}, \qquad (3.16)}$$

which is plotted as a function of N_d in Fig. 3.9.

The term proportional to N_d is negative when $S > 1$. This is the volume term with $\Delta\mu = \mu_l(P_v) - \mu_v(P_v)$, and it tells us how much lower energy the molecules would have in a bulk liquid under a flat surface (liquid pressure equal to vapour pressure), than they have in vapour. When $S > 1$ the stable phase is liquid and energy of the bulk liquid is lower.

The surface term proportional to $N_d^{2/3}$ is always positive (with $\sigma > 0$): this is the energy needed to build the interface between vapour and liquid. The surface energy is the reason why supersaturated vapour does not immediately turn to liquid. The sum of these two terms has a maximum at the *critical size* N_d^* when $S > 1$. This is seen more clearly in the upper panel of Fig. 3.10 where the surface and volume terms have been left out. The location and height of the maximum depends on S, as seen in the lower panel. For $S = 1$ the volume term is zero, and for $S < 1$ the volume term is also positive (vapour is the stable phase), and there is no maximum in the free energy curve which just continues to rise as a function of cluster size.

We were looking at the minimum in $\Delta\varphi$, but now we see that the equilibrium droplet is actually a maximum of $\Delta\varphi$. In the flat surface case we noted that we have to also require $\left(\frac{\partial^2 S}{\partial x^2}\right) = 0$, but we did not investigate the nature of extrema for the spherical surface case. The equilibrium droplet is in an unstable equilibrium: if the droplet size changes a little there is no mechanism to bring it back to the equilibrium size. If it shrinks a little it will get smaller and smaller until it has evaporated into vapour. If it grows a little its size increases uncontrollably (until the growth of the droplet has eaten up the vapour so that the saturation ratio has lowered to $S = 1$). Clusters smaller than the critical size $N_d < N_d^*$ tend to decay because the free energy hill goes down toward smaller sizes. But if somehow a cluster of size N_d^* manages to form, it tends to grow since downhill is now toward the larger sizes. The formation of critical clusters is *nucleation* and the formation rate is the *nucleation rate*, which describes how many clusters per unit time and volume grow over the hill top.

If there are pre-existing droplets, particles or microscopic surfaces on which vapour can condense, critical clusters form more easily, because the surface term is smaller (not a whole surface of a sphere is formed, but only some part of it as seen in Fig. 3.11). In this case nucleation is *heterogeneous*.

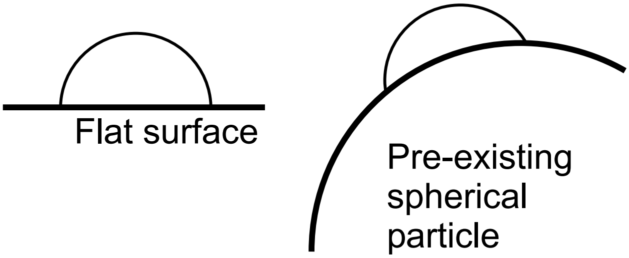


Fig. 3.11. Droplet formation on a pre-existing flat surface and spherical particle.

We first concentrate on homogeneous nucleation, where spherical droplets form in vapour without pre-existing concentration surfaces. Chapter 7 covers the basics of heterogeneous nucleation.

3.10 Treating non-equilibrium clusters

Strictly speaking our thermodynamic analysis and formula for $\Delta\varphi$ are not well defined for other sizes than the critical size: these are not equilibrium systems. To treat these non-equilibrium clusters thermodynamically, we have to apply some extra force field, which makes them stable. This could be imagined to be some kind of a cling film, hairnet or tweezers like in Fig. 3.12 which hold the droplet together and do not allow it to change size.

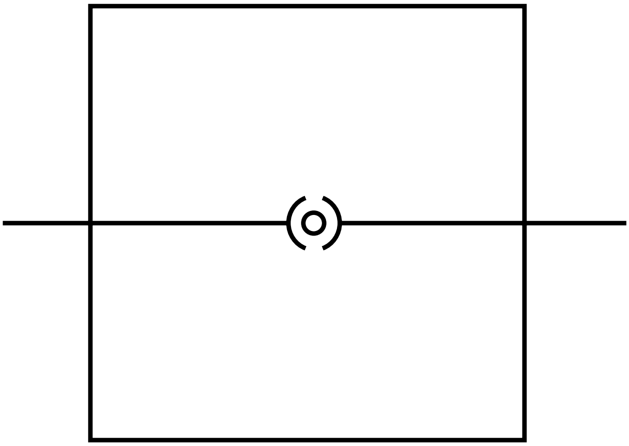


Fig. 3.12. Imaginary tweezers holding a non-equilibrium cluster together.

Another way around the problem is to assume that the droplet properties are independent of the surrounding vapour pressure: We search for the auxiliary vapour pressure $P'_g(N_d)$ where a cluster with N_d molecules is the critical cluster, calculate the formation energy in that vapour, and convert the result back to the real vapour.

The only term in eq. (3.16) that depends on the vapour pressure is $\Delta\mu$, since surface tension σ and molecular volume v_l for incompressible liquid are independent of the surroundings if temperature T is unchanged. Chemical potential difference in the auxiliary vapour is

$$\Delta\mu' = \mu_l(P'_g) - \mu_g(P'_g)$$

and in the real vapour

$$\Delta\mu = \mu_l(P_g) - \mu_g(P_g).$$

The difference between $\Delta\mu$ and auxiliary $\Delta\mu'$ can now be expressed as

$$\Delta\mu - \Delta\mu' = \mu_l(P_g) - \mu_l(P'_g) - [\mu_g(P_g) - \mu_g(P'_g)]. \tag{3.17}$$

We integrate the Maxwell equation (2.13) $d\mu = vdP$ in the gas (for ideal gas $PV = NkT_0$ and $v_g = \frac{kT_0}{P}$) leading to

$$\mu_g(P_g) - \mu_g(P'_g) = kT_0 \ln(\frac{P_g}{P'_g})$$

and in liquid (assumed incompressible, v_l = constant) resulting in

$$\mu_l(P_g) - \mu_l(P'_g) = v_l(P_g - P'_g).$$

Inserting these results for chemical potential differences in the gas and liquid into eq. (3.17) we get

$$\Delta\mu - \Delta\mu' = v_l(P_g - P'_g) - kT_0 \ln(\frac{P_g}{P'_g}) \tag{3.18}$$

In the auxiliary vapour the free energy of the critical N_d cluster is given by eq. (3.16)

$$\Delta\varphi' = -N_d kT_0 \ln S' + N_d^{2/3}\sigma(36\pi)^{1/3}v_l^{2/3}, \tag{3.19}$$

where $S' = \frac{P'_g}{P_e(T_0)}$. Now we assume that the only difference between the free energies is due to different gas phase pressures which affects both the liquid and gas chemical potentials in $\Delta\mu = \mu_l(P_g) - \mu_g(P_g)$ leading to

$$\Delta\varphi = \Delta\varphi' + N_d(\Delta\mu - \Delta\mu'). \tag{3.20}$$

Using equations (3.18) and (3.19) the formation free energy in the real vapour can be written as

$$\begin{aligned}\Delta\varphi = &- N_d kT_0 \ln \frac{P'_g}{P_e(T_0)} + N_d^{2/3}\sigma(36\pi)^{1/3}v_l^{2/3} \\ &+ N_d\left(v_l(P_g - P'_g) - kT_0 \ln(\frac{P_g}{P'_g})\right),\end{aligned} \tag{3.21}$$

which simplifies to

$$\Delta\varphi = kT_0 \ln \frac{P_g}{P_e(T_0)} + v_l(P_g - P'_g) + N_d^{2/3}\sigma(36\pi)^{1/3}v_l^{2/3}, \tag{3.22}$$

where $P_g/P_e(T_0) = S$. We have already shown that $v_l(P_g - P'_g)$ term is small compared to $kT_0 \ln S$ (see p. 30) and indeed we get with a good accuracy also for non-equilibrium clusters

$$\Delta\varphi = -N_d kT_0 \ln S + N_d^{2/3}\sigma(36\pi)^{1/3}v_l^{2/3},$$

which means that the curves in Figures 3.9 and 3.10 are justified.

3.11 Free energy barrier in the Ising model

As a reminder that any first-order phase transition can be treated with the same machinery as a gas-liquid transition, we have a look at a phase transition in a magnetic system, and show that the formation free energy curves are similar to those drawn in section 3.9.

We have an array of spins in a magnetic field with magnetic flux density $\mathcal{B}$ directed along the z-axis as in Fig. 3.13. All the spins would like to point to the same direction with the field when $|\mathcal{B}| > 0$. The stable phase is all up (or down), but the energy barrier hinders this. When $\mathcal{B} = 0$, the stable phase would be totally random orientations with as many spins up and down. If only nearest neighbour interactions are taken into account, this system is called the Ising model. In the basic Ising system the spins are arranged as a cubic lattice in one, two or three dimensions. The energy in the Ising model is

$$E = -\varepsilon \sum_{<lm>} s_l s_m + kTb \sum_l s_l, \tag{3.23}$$

where $< lm >$ denotes a summation over nearest neighbours with each pair counted only once, ε is the spin-spin coupling constant, and h is the parameter describing the interaction with an external field ($b = \mu_s \mathcal{B}/(kT)$, where μ_s is the magnetic dipole moment of the spin particles). The value of the z-component of the spins, s_l, is restricted to ± 1. For a three-dimensional cubic lattice the coupling constant may be expressed in terms of the numerically determined critical temperature T_c according to $\varepsilon/(kT_c) = 0.221656$, where T_c marks the transition temperature between the ferromagnetic and paramagnetic states at $\mathcal{B} = 0$. We see from eq. (3.23) that if the neighbouring spins are both up ($s_l = +1$) or both down ($s_l = -1$), the contribution to energy is $-\varepsilon$, but if one is up and one is down, the contribution is $+\varepsilon$. Thus the surface between regions of up spins and down spins leads to increased energy just like surface tension.

Here we look at a three-dimensional Ising lattice with the magnetic field $\mathcal{B}$ pointing up. The free energy of formation of a region of i up spins in a lattice where the all the spins are originally down is given by

$$\Delta\varphi/(kT) = \zeta i^{2/3} - 2bi,$$

where ζ is related to the surface σ tension via $\zeta = (36\pi)^{1/3}\sigma/(kT)$ (Heermann et al. 1984). The number of spins on the surface of the "up" region containing i spins is for a spherical cluster proportional to $i^{2/3}$.
Fig. 3.14 shows the free energy as a function of cluster size for two magnetic field strengths corresponding to $b = 0.3$ and $b = 0.25$ with critical cluster sizes 37 and 65, respectively.

The Ising model is easy to study by computer simulations. Thus, Ising model nucleation has been extensively simulated and the results have been

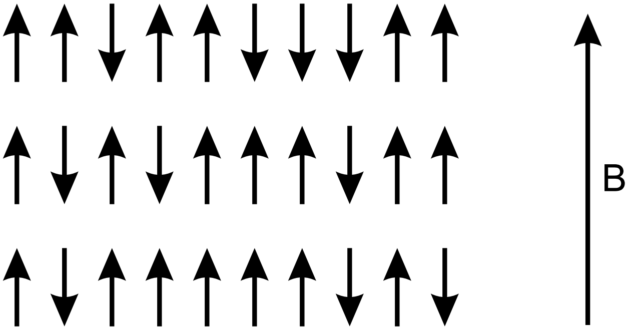


Fig. 3.13. Schematic figure of array of spins in a magnetic field $\mathcal{B}$.

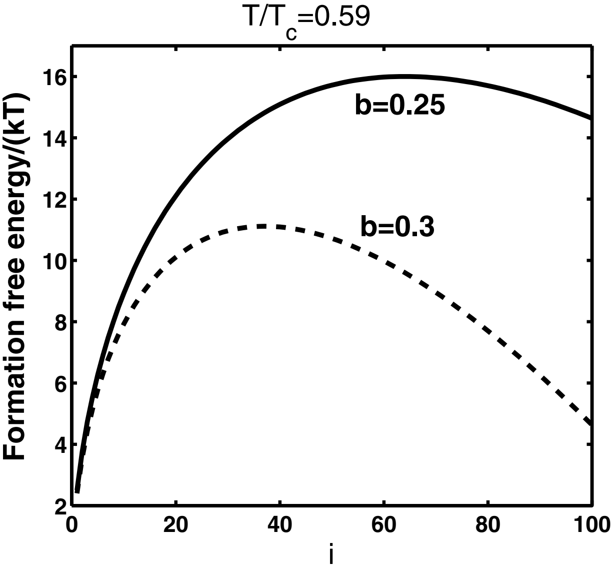


Fig. 3.14. Formation free energy as a function of the cluster size for two magnetic field values in a three dimensional Ising model. For temperature $T/T_c = 0.59$ surface tension parameter has the value $\zeta = 3$ (Heermann et al. 1984).

compared to classical theory predictions (Heermann et al. 1984; Wonczak et al. 2000; Acharyya and Stauffer 1998; Vehkamäki and Ford 1999).

3.12 Multicomponent case

Now we develop a practicable formula for the formation free energy as a function of the number of molecules for a multicomponent cluster. We start again with eq. (3.15)

$$\Delta\varphi = \sum \Delta\mu_i N_{i,l} + \sigma A + \sum(\mu_{i,s} - \mu^0_{i,g})N_{i,s}.$$

Now the chemical potential difference $\Delta\mu_i$ and surface tension σ are functions of mole fractions

$$x_{i,l} = \frac{N_{i,l}}{\sum N_{j,l}}$$

and $N_{i,s} \neq 0$ even for equimolar surface and we have to deal with them as well as the chemical potential difference $(\mu_{i,s} - \mu^0_{i,g})$, which fortunately disappeared from the free energy formula in the one-component system.

For non-critical clusters $\mu_{i,s} \neq \mu^0_{i,g}$, but we have to assume that $\mu_{i,s} = \mu_{i,l}(P_l, x_{i,l})$ to proceed. This assumption is justified if the diffusion between the surface and the "core" of the cluster is much faster compared to the diffusion between the droplet and the original phase, which is normally the case in vapour-liquid nucleation. Now the familiar integral of the Maxwell equation (2.13) for an incompressible liquid gives $\mu_{i,l}(P_l, x_{i,l}) = \mu_{i,l}(P_g, x_{i,l}) + v_{i,l}(P_l - P_g)$ and we can express the chemical potential difference $(\mu_{i,s} - \mu^0_{i,g})$ as

$$\begin{aligned}\mu_{i,s} - \mu^0_{i,g} &= \mu_{i,l}(P_l, x_{i,l}) - \mu^0_{i,g} \\ &= \mu_{i,l}(P_g, x_{i,l}) + v_{i,l}(P_l - P_g) - \mu^0_{i,g} \\ &= \Delta\mu + v_{i,l}(P_l - P_g)\end{aligned}$$

with the definition (2.14) $\Delta\mu \equiv \mu_{i,l}(P_g, x_{i,l}) - \mu^0_{i,g}$.

Again we have to find a vapour pressure P'_g at which our cluster is critical: Only then is eq. (3.15) really justified and phase equilibrium gives the pressure difference as

$$v_{i,l}(P_l - P'_g) = \frac{2\sigma v_{i,l}}{r}$$

according to the Laplace equation (2.8). We make the ideal gas assumption to get $\Delta\mu' = -kT_0 \ln \frac{\mathcal{A}'_{i,g}}{\mathcal{A}_{i,l}(x_{i,l})}$. As in the one-component case, we assume cluster properties independent of the surrounding vapour and convert back to $P_{i,g}$ just like in the one-component case on p. 66. If we neglect again the small terms $v_{i,l}(P_g - P'_g)$ we see that eq. (3.15) is very accurately valid also for non-equilibrium clusters and the difference in chemical potentials is given by

$$\mu_{i,s} - \mu^0_{i,g} = \Delta\mu_i + \frac{2\sigma(x_{i,g})v_{i,l}(x_{i,l})}{r} \tag{3.24}$$

where

$$\Delta\mu_i = -kT_0 \ln \frac{\mathcal{A}_{i,g}}{\mathcal{A}_{i,l}(x_{i,l})}.$$

Now we know almost everything needed to plot the formation free energy using eq. (3.15). Only the surface excess numbers $N_{i,s}$, $i = 1, ..., n$ are left to calculate. We need n conditions to find these unknown numbers. One is the equimolar surface condition (3.13)

$$\sum N_{s,i} v_{l,i}(x_{i,l}) = 0. \tag{3.25}$$

The Gibbs adsorption isotherm (1.12)

$$\sum d\mu_{i,s} N_{i,s} + A d\sigma = 0$$

gives $n-1$ equations in the following way: we assumed $d\mu_{i,s} = d\mu_{i,l}(P_l, x_{i,l})$ and the liquid is characterised by $n-1$ mole fractions $x_{j,l}$. The derivatives in the Gibbs adsorption isotherm can be taken with respect to any of these mole fractions

$$\sum_i N_{i,s} \left(\frac{\partial \mu_{i,s}}{\partial x_{j,l}} \right)_{x_{k \neq j,l}, r} + A \left(\frac{\partial \sigma}{\partial x_{j,l}} \right)_{x_{k \neq j,l}, r} = 0, \tag{3.26}$$

for $j = 1, ... n-1$. Surface phase chemical potentials $\mu_{i,s}$ can be calculated from eq. (3.24) as

$$\mu_{i,s} = \mu_{i,l} = \mu_{i,g}^0 + \Delta\mu_i + \frac{2\sigma(x_{i,g}) v_{i,l}(x_{i,l})}{r},$$

where $\mu_{i,g}^0$ is just a constant with respect to the liquid mole fractions. The chemical potential derivatives required for equations (3.26) are

$$\begin{aligned} \left(\frac{\partial \mu_{i,s}}{\partial x_{j,l}} \right)_{x_{k \neq j,l}, r} &= \left(\frac{\partial \mu_{i,l}}{\partial x_{j,l}} \right)_{x_{k \neq j,l}, r} \\ &= \left(\frac{\partial \Delta\mu_i}{\partial x_{j,l}} \right)_{x_{k \neq j,l}} + \frac{2\sigma}{r} \left(\frac{\partial v_{i,l}}{\partial x_{j,l}} \right)_{x_{k \neq j,l}} + \frac{2 v_{i,l}}{r} \left(\frac{\partial \sigma}{\partial x_{j,l}} \right)_{x_{k \neq j,l}}, \end{aligned} \tag{3.27}$$

where the last term containing the derivative of the surface tension is usually numerically so small that it can be neglected.

For two-component systems ($n = 2$) the solution of equations (3.26) and (3.25) is (Laaksonen et al. 1999; Noppel et al. 2002)

$$\begin{aligned} N_{2,s} &= \frac{A \dfrac{d\sigma}{dx_{2,l}}}{\dfrac{v_{2,l}}{v_{1,l}} \left(\dfrac{\partial \mu_{1,l}}{\partial x_{2,l}} \right) - \left(\dfrac{\partial \mu_{2,l}}{\partial x_{2,l}} \right)} \\ N_{1,s} &= \frac{A \dfrac{d\sigma}{dx_{2,l}}}{\dfrac{v_{1,l}}{v_{2,l}} \left(\dfrac{\partial \mu_{2,l}}{\partial x_{2,l}} \right) - \left(\dfrac{\partial \mu_{1,l}}{\partial x_{2,l}} \right)}. \end{aligned} \tag{3.28}$$

The formation free energy in eq. (3.15) can be simplified using eq. (3.24) in the following way

$$\begin{aligned}\Delta\varphi &= \sum \Delta\mu_i N_{i,l} + \sigma A + \sum(\mu_{i,s} - \mu_{i,g}^0)N_{i,s}\\ &= \sum \Delta\mu_i N_{i,l} + \sigma A + \sum \left(\Delta\mu_i + \frac{2\sigma v_{i,l}}{R}\right)N_{i,s}\\ &= \sum \Delta\mu_i \big(N_{i,l} + N_{i,s}\big) + \sigma A + \frac{2\sigma}{R}\sum v_{i,l}N_{i,s}\end{aligned}$$

$$\boxed{\Delta\varphi = \sum_i \Delta\mu_i N_{i,d} + \sigma A,} \tag{3.29}$$

since $\sum v_{i,l}N_{i,s} = 0$ for an equimolar surface (3.13). For an ideal gas mixture and incompressible liquid, $\Delta\mu$ is given by eq. (2.20) and the formation free energy (3.29) has the form

$$\boxed{\Delta\varphi = -kT\sum_i \ln\left(\frac{\mathcal{A}_{i,g}}{\mathcal{A}_{i,l}(x_{i,l})}\right)N_{i,d} + \sigma A.} \tag{3.30}$$

Now it looks as if we needed to know only the total number of cluster molecules $N_{i,d}$, and the division to core $N_{i,l}$ and surface excess numbers $N_{i,s}$ would be irrelevant, but this is a crucial mistake: the chemical potential difference $\Delta\mu_i = \Delta\mu_i(x_{i,l})$ (or liquid phase activity $\mathcal{A}_{i,l}(x_{i,l})$), surface tension $\sigma = \sigma(x_{i,l})$ and partial molecular volumes $v_l = v_l(x_{i,l})$ depend on the bulk mole fractions $x_{i,l} = \frac{N_{i,l}}{\sum N_{i,l}} \neq \frac{N_{i,d}}{\sum N_{i,d}}$ and the difference (unfortunately) matters. Also the partial molecular volumes enter the free energy of formation via the surface area A

$$A = 4\pi r^2 = 4\pi\big(\frac{3V}{4\pi}^{2/3}\big) = (36\pi)^{1/3}\big[\sum v_{i,l}(x_{i,l})N_{i,l}\big]^{2/3}$$

and we need $x_{i,l}$, and thus $N_{i,l}$ here as well (although $\sum v_{i,l}N_{i,l} = \sum v_{i,l}N_{i,d}$ for an equimolar surface).

We are ready to draw free energy as a function of $N_{i,d}$ (or $N_{i,l}$) (in the two-component system for simplicity):

1. Select the core molecular numbers $N_{1,l}, N_{2,l}$.
2. Calculate the core mole fraction $x_{2,l} = \dfrac{N_{2,l}}{N_{1,l} + N_{2,l}}$.
3. Solve for the surface excess numbers $N_{2,s}$ and $N_{2,s}$ from equations (3.28) using equations (3.27) for the chemical potential derivatives. If the surface excess numbers are not small compared to core numbers, the theory is probably falling apart.
4. Put it all together and you get $N_{1,d}, N_{2,d}, \Delta\varphi$.
5. Repeat for several $N_{1,l}, N_{2,l}$ and plot $\Delta\varphi$ as a function of $N_{1,d}$ and $N_{2,d}$.

In the two-component case the surface of $\Delta\varphi(N_{1,d}, N_{2,d})$ is a saddle surface and the critical cluster is identified as the *saddle point* of the surface. This means that in one direction the point is a maximum and in the perpendicular direction(s) it is a minimum. If there are more components, the critical size is a maximum in only one direction, and a minimum in other directions.

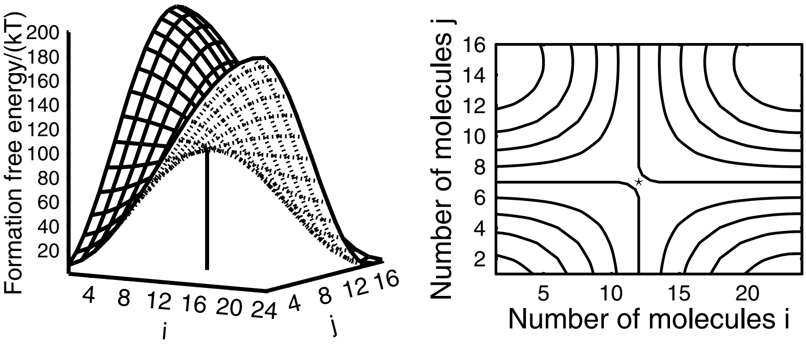


Fig. 3.15. Formation free energy as a function of the numbers of molecules of two components. The left-hand figure shows the three-dimensional surface and the right-hand figure is a contour plot of the same surface. Critical size is marked with a vertical line in the surface plot and a star in in contour plot.

If you use erroneously

$$x_{2,l} = \frac{N_{2,d}}{N_{1,d} + N_{2,d}}$$

the figure gives a different (and wrong) critical cluster compared to the equilibrium conditions (2.23) and (2.24)

$$\frac{\Delta\mu_1}{v_{1,l}} = \frac{\Delta\mu_2}{v_{2,l}}$$

$$r = \frac{2\sigma v_{1,l}}{\Delta\mu_1}$$

A similar error is made if you use $\Delta\varphi = \sum_i \Delta\mu_i N_{i,l} + \sigma A$ instead of $\Delta\varphi = \sum_i \Delta\mu_i N_{i,d} + \sigma A$, and take the derivative of this with respect to $N_{i,l}$ to derive the equilibrium conditions (see p. 54). In this case you are left with a derivative of surface tension in the equilibrium conditions, because there are no surface excess molecules and you cannot use a Gibbs adsorption isotherm to get rid of this derivative. Instead of the correct Kelvin equation (2.15) you end up with $\Delta\mu_i + \frac{2\sigma v_{i,l}}{r} + 4\pi r^2 \left(\frac{\partial\sigma}{\partial N_i}\right) = 0$, and the surface tension derivative will appear also in equations for composition (2.23) and radius (2.24) of the critical cluster, which are just differently arranged Kelvin equations. The theory where surface tension derivatives cancel is often referred to as the revised theory, and it has been proved to be the thermodynamically consistent version by several authors (Flood 1934; Volmer 1939; Neumann and Döring 1940; Reiss 1950; Nishioka and Kusaka 1992; Wilemski 1984; Renninger et al. 1981; Wilemski 1987; Mirabel and Reiss 1987; Laaksonen et al. 1993).

An example of the consequences of neglecting the surface excess molecules is given by Fig. 3.16 describing the free formation free energy surface in a water-ethanol system. The critical size (172 water molecules, 26 ethanol molecules) given by the equilibrium conditions (2.23) and (2.24) is marked also in the figure. The molecular number in the horizontal and vertical axes are the core numbers $N_{i,l}$. If you neglect the contribution of the surface excess molecules, you get a free energy surface which would suggest a critical size around 70 water molecules, and 35 ethanol molecules, but this point does not satisfy the equilibrium conditions (2.23) and (2.24).

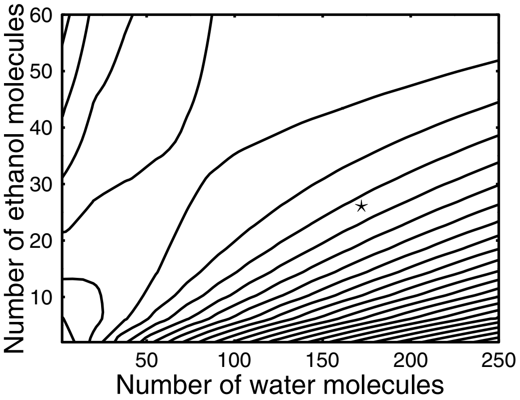


Fig. 3.16. The free energy surface for water-ethanol mixture with the surface excess molecules neglected. Temperature is T=260K, gas phase activities of the two components are equal $\mathcal{A}_{1,g} = \mathcal{A}_{2,g} = 1.5$. The critical size (172 water molecules, 26 ethanol molecules) given by the equilibrium conditions (2.23) and (2.24) is marked with a star. The horizontal and vertical axes show the core numbers $N_{i,l}$.

Unfortunately the water-ethanol system is so strongly surface active that classical theory breaks down: if we try to calculate the surface excess numbers they turn out to be large and fluctuating, so that it is not possible to plot the correct free energy surface where the axes would correspond to total (core and surface excess) numbers. If such a surface could be plotted, the saddle point would be in the correct place given by the equilibrium conditions.

3.13 Consistency issues

Expressions (3.16), (3.29) and (3.30) suffer from self-consistency problems: They do not give zero formation free energy for a single molecule. This is easily seen in one-component saturated vapour, where $S = 1$ and the volume term gives zero, but the surface term is non-zero. Another inconsistency is that if we reach the spinodal the formation free energy should vanish, but the classical results give again a non-zero free energy barrier even for the spinodal conditions.

3.14 Summary of free energies for droplet formation

- If you assume that the droplet is small compared to the vapour phase and its formation does not affect the vapour pressure or composition, you can use either the Helmholtz free energy, the Gibbs free energy or the grand potential as the free energy.
- The numbers of molecules in the droplet $N_{i,d}$ are calculated as the sum of hypothetical bulk liquid values $N_{i,l}$ and surface excess correction terms $N_{i,s}$. The division between these two terms is arbitrary and depends on the chosen position of the dividing surface. In classical theory we have to assume that the dividing surface is the equimolar surface and that it coincides with the surface of tension. This assumption is equivalent to using curvature independent surface tension. Such an assumption is not justified in surface active mixtures, and causes sometimes unphysical predictions. In a more general description the surface of tension and the equimolar surface do not coincide, and the distance between these two dividing surfaces is called Tolman's length (Tolman 1949), which determines the first curvature correction to surface tension.
- The general form for droplet formation free energy is

$$\Delta\varphi = \sum \Delta\mu_i N_{i,d} + \sigma A$$

  with $\Delta\mu = -kT \frac{\mathcal{A}_{i,g}}{\mathcal{A}_{i,l}(x_{i,l})}$ for an ideal mixture of ideal gases. It must be noted that activity, surface tension and density (which is needed to calculate area A) can not be directly calculated from total numbers of molecules in the droplet $N_{i,d}$, but the bulk liquid numbers $N_{i,l}$ must be solved first.
- In a one-component system the formation free energy takes the form

$$\Delta\varphi = -N_d k T_0 \ln S + N_d^{2/3} \sigma (36\pi)^{1/3} v_l^{2/3}.$$

- The formulae above can be used also for non-equilibrium clusters, although strictly speaking the thermodynamic machinery we have used is applicable only to equilibrium systems. Thus you can plot the free energy for different cluster sizes and compositions using these equations.

- For a critical cluster the formation energy is given by

$$\Delta\varphi^* = \frac{4}{3}\pi\sigma^* r^{*2}.$$

Problems

3.1. For the constant temperature case the free energy change in droplet formation is $\Delta\varphi = (P_g^0 - P_l)V + A\sigma + \sum_i(\mu_{i,l} - \mu_{i,g}^0)N_{i,l} + \sum_i(\mu_{i,s} - \mu_{i,g}^0)N_{i,s}$. Derive conditions for the equilibrium droplet by
– taking the differential with respect to $N_{i,l}$ keeping $N_{j\neq i,l}$, $N_{i,s}$ and V constant
– taking the differential with respect to $N_{i,s}$ keeping $N_{i,l}$, $N_{j\neq i,s}$ and V constant
– taking the differential with respect to V keeping $N_{i,l}$ and $N_{i,s}$ constant.
The last derivative means moving the hypothetical dividing surface, but keeping the real physical properties of the cluster unchanged. You need the Gibbs-Duhem equation, the Gibbs adsorption isotherm and definition of the surface of tension to obtain the familiar equilibrium conditions. Quantities with superscript ^{0} are always constants.

3.2. Derive a compressibility-corrected Kelvin equation assuming that the liquid density increases linearly with increasing pressure $\rho_l = \rho_0 + \alpha(P_l - P_0)$, where ρ_0, P_0 and α are constants.

3.3. Plot the radius of an equilibrium cluster in pure water vapour as a function of
a) relative humidity at temperature 298K.
b) temperature with constant relative humidity 500%.
c) temperature with constant vapour concentration ρ_g=6.33 mol/m^3.

The saturation vapour pressure of water is (T in Kelvin)
$P_e = \exp[77.34 - 7235.42/T - 8.2\ln(T) + 0.00571T]$ Pa.
Density of liquid water is
$\rho_l = (1049.572 - 0.1763T)$ kg/m^3.
Molar mass of water is 18.02 g/mol.
Surface tension of pure water is
$\sigma = (0.117 - 0.152\cdot 10^{-3}T\ )$ N/m.
Water vapour is assumed to be an ideal gas, and liquid is assumed incompressible.

3.4. The formation free energy of a cluster is $\Delta\varphi = A\sigma + \sum_i \Delta\mu N_{i,d}$. Express this in terms of the a) cluster radius r b) numbers of molecules in the cluster $N_{i,d}$ for multicomponent systems (you do not have to do anything to the chemical potential difference $\Delta\mu$ and surface tension σ, just manipulate the surface area A and $N_{i,d}$ appropriately).

3.5. Plot the free energy curves for water at temperatures 280K, 300K and 320K with saturation ratios S=2, 5 and 10.

The saturation vapour pressure of water is (T in Kelvin)
$P_e = \exp[77.34 - 7235.42/T - 8.2\ln(T) + 0.00571T]$ Pa.
Density of liquid water is
$\rho_l = (1049.572 - 0.1763T)$ kg/m^3.
Molar mass of water is 18.02 g/mol. Surface tension of pure water is
$\sigma = (0.117 - 0.152 \cdot 10^{-3}T\ )$ N/m.
Water vapour is assumed to be an ideal gas, and liquid is assumed incompressible.

3.6. Consider a two-component system.
a) Show that if you take the formation free energy of a cluster to be $\Delta\varphi = \sum_{i=1}^{2} \Delta\mu_i N_{i,l} + \sigma A$, and derive equilibrium conditions by taking the partial derivatives of the formation free energy with respect to $N_{1,l}$ and $N_{2,l}$, you get conditions
$\Delta\mu_1 + \dfrac{2\sigma v_{1,l}}{r} - 4\pi r^2 \left(\frac{\partial\sigma}{\partial x}\right) x \frac{1}{N_{1,l}+N_{2,l}} = 0$ and
$\Delta\mu_2 + \dfrac{2\sigma v_{2,l}}{r} + 4\pi r^2 \left(\frac{\partial\sigma}{\partial x}\right) (1-x) \frac{1}{N_{1,l}+N_{2,l}} = 0$,
where $x = \frac{N_{2,l}}{N_{1,l}+N_{2,l}}$.
b) Solve this pair of equations for $N_{1,l}$ and $N_{2,l}$ in water-ethanol system at 260K and $\mathcal{A}_w$=$\mathcal{A}_e$=1.5. Compare the critical cluster size you obtain with the saddle surface in Fig. 3.16.

The saturation vapour pressures of water and ethanol are (Pa, T in Kelvin):
$P^o_{w,e} = \exp[77.34 - 7235.42/T - 8.2\ln(T) + 0.00571T]$ and
$P^o_{e,e} = 6.137 \cdot 10^6$
$\cdot \exp\{[-8.4565739(1 - T/513.92) + 0.090430576(1 - T/513.92)^{1.5}$
$-4.83483(1 - T/513.92)^3 + 3.7610779(1 - T/513.92)^6]513.92/T\}$.
At T=260K liquid phase activities are
$\mathcal{A}_{w,l} = (1-x)10^{0.4x^2/(x+(0.4(1-x))/0.64)^2}$
$\mathcal{A}_{e,l} = x10^{0.64(1-x)^2/(1-x+(0.64x)/0.4)^2}$.
At T=260K liquid density is [kg/m^3]
$\rho_l = 1000 \cdot (0.997056 - 0.127749x - 0.447381x^2 + 0.716194x^3 - 0.320963x^4)$.
Surface tension of the mixture is (N/m, T in Kelvin)
$\sigma = 0.001 \cdot \exp[4.821 - 0.00188T + (2.775 - 0.01955T)y$
$+(-19.04 + 0.07446T)y^2 + (27.47 - 0.09442T)y^3 + (-11.78 + 0.03748T)y^4]$,
where $y = 4x/(1+3x)$, x is the mole fraction of ethanol.
Molar mass of water is 18.02 g/mol and that of ethanol 46.07 g/mol.
Vapour assumed to be an ideal gas, liquid assumed incompressible.

4

Equilibrium cluster distribution

So far we have studied one cluster forming in a vapour. Now we want to calculate the cluster distribution in an equilibrium vapour (Frenkel 1939; Abraham 1974). Let the number concentration [1/m^3] of clusters of composition $\{N_{i,l}\} = (N_{1,d}, N_{2,d}, N_{3,d}, \cdots)$ be $C(\{N_{i,d}\})$. This cluster has for example $N_{1,d}$ water molecules, $N_{2,d}$ sulphuric acid molecules, $N_{3,d}$ ammonia molecules and so on. When one component, say that with index k, needs to be highlighted in the derivation, we write the cluster composition as $\{N_{i,d}\} = \{N_{i,d}, N_{k,d}\}$.

We treat the formation (and break-up) of clusters as a series of chemical reactions

$$M_k + D(\{N_{i,d}, N_{k,d}\}) \leftrightarrows D(\{N_{i,d}, N_{k,d} + 1\}) \tag{4.1}$$

where M_k stand for single molecule, *monomer*, of substance k and $D(\{N_{i,d}, N_{k,d}\})$ stands for a droplet/cluster with composition $\{N_{i,d}, N_{k,d}\}$. We take this chemical reaction to occur at constant total pressure P_0 and constant temperature T_0, and with constant total number of molecules of each type. According to p. 45 the suitable potential which should have a minimum in equilibrium is the Gibbs free energy.

We treat the mixture of monomers and clusters of all sizes as an ideal mixture of ideal gases. The energy of the mixture is

$$U = T_0\mathcal{S} - P_0V + \sum_{\text{clusters}} \mu(\{N_{i,d}\})VC(\{N_{i,d}\}),$$

where the summation goes over all cluster types including monomers. Chemical potential $\mu(\{N_{i,d}\})$ is the increase in energy of the system when one cluster of size $\{N_{i,d}\}$ is added to it. The Gibbs free energy per volume unit g_v is

$$g_v \equiv \frac{G}{V} = \frac{U - T_0\mathcal{S} + P_0V}{V} = \sum_{\text{clusters}} \mu(\{N_{i,d}\})C(\{N_{i,d}\}),$$

and the equilibrium cluster distribution is obtained by finding the cluster concentrations $C^e(\{N_{i,d}\})$ for which g_v has a minimum.

The chemical potential $\mu(\{N_{i,d}\})$ depends on the concentration of clusters $\{N_{i,d}\}$ via (see eq. 2.21, p. 30)

$$\mu(\{N_{i,d}\}) = \mu^{p,P_0}(\{N_{i,d}\}) + kT \ln \frac{C(\{N_{i,d}\})}{C_{\text{tot}}},$$

where the total number of clusters (including monomers) is

$$C_{\text{tot}} = \sum_{\text{clusters}} C(\{N_{i,d}\}) \tag{4.2}$$

and $\mu^{p,P_0}(\{N_{i,d}\})$ is the chemical potential of $\{N_{i,d}\}$ clusters in a gas consisting solely of them at pressure $P_0 = kTC_{\text{tot}}$, and thus independent of concentration $C(\{N_{i,d}\})$. When monomers join the cluster the total number of clusters decreases but the volume of the container is adjusted so that the concentration of clusters C_{tot} and the pressure P_0 stay constant.

Now we are ready to find the minimum by setting the differential of Gibbs free energy

$$g_v = \sum_{\text{clusters}} \mu^{p,P_0}(\{N_{i,d}\}) C(\{N_{i,d}\}) + kT \sum_{\text{clusters}} C(\{N_{i,d}\}) \ln \frac{C(\{N_{i,d}\})}{C_{\text{tot}}}$$

to zero. We perform the variations of the concentrations by letting reactions (4.1) occur from left to right: for the three cluster types involved, the changes of concentrations are related as

$$dC_{k,\text{mon}} : dC(\{N_{i,d}, N_{k,d}\}) : dC(\{N_{i,d}, N_{k,d}+1\}) = -1 : -1 : 1, \tag{4.3}$$

where $C_{k,\text{mon}}$ is the concentration of monomers of type k. All the other cluster concentrations are unchanged. In the case of a pure *dimer* $\{N_{i,d}\} = (0, 0, \cdots, 2, \cdots, 0, 0)$ (a cluster with two molecules, both of the same type) formation there are only two cluster types involved, and the relation is

$$dC_{k,\text{mon}} : dC((0, 0, \cdots, 2, \cdots, 0, 0)) = -2 : 1. \tag{4.4}$$

By collecting the terms proportional to $dC(\{N_{i,d}\}$ under the first summations we get for the change of Gibbs free energy

$$\begin{aligned} dg_v = &\sum_{\text{clusters}} \left(\mu^{p,P_0}(\{N_{i,d}\}) + kT \ln \frac{C^e(\{N_{i,d}\})}{{C^e}_{\text{tot}}} \right) dC^e(\{N_{i,d}\}) \\ &+ kT \sum_{\text{clusters}} C^e(\{N_{i,d}\}) d \left(\ln \frac{C^e(\{N_{i,d}\})}{{C^e}_{\text{tot}}} \right) = 0. \end{aligned} \tag{4.5}$$

Now we first show that the second summation in eq. (4.5) yields zero:

$$
\begin{aligned}
&\sum_{\text{clusters}} C^e(\{N_{i,d}\}) d \left(\ln \frac{C^e(\{N_{i,d}\})}{{C^e}_{\text{tot}}} \right) \\
&= \sum_{\text{clusters}} C^e(\{N_{i,d}\}) \frac{{C^e}_{\text{tot}}}{C^e(\{N_{i,d}\})} \left(\frac{{C^e}_{\text{tot}} dC^e(\{N_{i,d}\}) - C^e(\{N_{i,d}\}) d{C^e}_{\text{tot}}}{({C^e}_{\text{tot}})^2} \right) \\
&= \sum_{\text{clusters}} dC^e(\{N_{i,d}\}) - \frac{C^e(\{N_{i,d}\})}{{C^e}_{\text{tot}}} d{C^e}_{\text{tot}} \\
&= \sum_{\text{clusters}} dC^e(\{N_{i,d}\}) - \frac{d{C^e}_{\text{tot}}}{{C^e}_{\text{tot}}} \underbrace{\sum_{\text{clusters}} C^e(\{N_{i,d}\})}_{{C^e}_{\text{tot}}} \\
&= \sum_{\text{clusters}} dC^e(\{N_{i,d}\}) - d{C^e}_{\text{tot}}.
\end{aligned}
$$

We have used the fact that ${C^e}_{\text{tot}}$ and its differential are independent of the summation indices and can thus be taken outside the summations. By using the differential of relation (4.2) for total number of clusters we note that this term indeed vanishes.

In the first sum of derivative (4.5) only three terms (two in the case of pure dimer formation) corresponding to the product and reactants of reaction (4.1) are non-zero. Using relation (4.3) for the concentration differentials we get

$$
\begin{aligned}
dg_v = &- \mu^{p,P_0}(\{N_{i,d}\}) - kT \ln \frac{C^e(\{N_{i,d}\})}{{C^e}_{\text{tot}}} + \mu^{p,P_0}(\{N_{i,d}, N_{k,d}+1\}) \\
&+ kT \ln \frac{C^e(\{N_{i,d}, N_{k,d}+1\})}{{C^e}_{\text{tot}}} - \mu^{p,P_0}_{k,\text{mon}} - kT \ln \frac{C^e_{k,\text{mon}}}{{C^e}_{\text{tot}}} = 0,
\end{aligned}
$$

which can be rearranged to give

$$
\begin{aligned}
&kT \ln \frac{C^e(\{N_{i,d}, N_{k,d}+1\})}{C^e(\{N_{i,d}, N_{k,d}\})} \\
&\quad = kT \ln \frac{C^e_{k,\text{mon}}}{{C^e}_{\text{tot}}} - [\mu^{p,P_0}(\{N_{i,d}, N_{k,d}+1\}) - \mu^{p,P_0}(\{N_{i,d}, N_{k,d}\}) - \mu^{p,P_0}_{k,\text{mon}}],
\end{aligned}
$$

which gives a formula for the equilibrium concentration of the product of the growth reaction (4.1)

$$
\begin{aligned}
&C^e(\{N_{i,d}, N_{k,d}+1\}) = C^e(\{N_{i,d}, N_{k,d}\}) \frac{C^e_{k,\text{mon}}}{{C^e}_{\text{tot}}} \\
&\quad \cdot \exp \left[-\frac{1}{kT} \left(\mu^{p,P_0}(\{N_{i,d}, N_{k,d}+1\}) - \mu^{p,P_0}(\{N_{i,d}, N_{k,d}\}) - \mu^{p,P_0}_{k,\text{mon}} \right) \right].
\end{aligned}
\tag{4.6}
$$

In the case of dimer formation only two terms in the sum (4.5) are non-zero:

$$\begin{aligned} dg_v =&\mu^{p,P_0}((0,\cdots,2,\cdots,0)) + kT\ln\frac{C^e((0,\cdots,2,\cdots,0))}{{C^e}_{\text{tot}}} \\ &- 2\left(\mu^{p,P_0}_{k,\text{mon}} + kT\ln\frac{C^e_{k,\text{mon}}}{C^e_{\text{tot}}}\right) = 0, \end{aligned}$$

which leads to

$$\begin{aligned} &C^e((0,\cdots,2,\cdots,0)) = \\ &\quad\frac{(C^e_{k,\text{mon}})^2}{C^e_{\text{tot}}}\exp\left[-\frac{1}{kT}\left(\mu^{p,P_0}((0,\cdots,2,\cdots,0)) - 2\mu^{p,P_0}_{k,\text{mon}}\right)\right]. \end{aligned} \tag{4.7}$$

Eq. (4.6) actually reduces to (4.7) when the reaction occurs between two similar monomers.

We can build any cluster one by one from monomers applying eq. (4.6) successively and we get the equilibrium cluster distribution in an n-component system

$$\boxed{\begin{aligned} C^e(\{N_{i,d}\}) = {C^e}_{\text{tot}}&\left(\frac{C^e_{1,\text{mon}}}{{C^e}_{\text{tot}}}\right)^{N_{1,d}}\cdots\left(\frac{C^e_{i,\text{mon}}}{{C^e}_{\text{tot}}}\right)^{N_{i,d}}\cdots\left(\frac{C^e_{n,\text{mon}}}{{C^e}_{\text{tot}}}\right)^{N_{n,d}} \\ &\cdot\exp\left\{-\frac{1}{kT}\left[\mu^{p,P_0}(\{N_{i,d}\}) - \sum_{i=1}^{n} N_{i,d}\mu^{p,P_0}_{i,\text{mon}}\right]\right\}. \end{aligned}} \tag{4.8}$$

Result (4.8) can be written in the form of *law of mass action.* It is important to note that the exponential is independent of the partial pressures of monomers, and the monomer pressure dependences can be separated out as

$$C^e(\{N_{i,d}\}) = (C^e_{1,\text{mon}})^{N_{1,d}}\cdots(C^e_{i,\text{mon}})^{N_{i,d}}\cdots(C^e_{n,\text{mon}})^{N_{n,d}}K(T_0,P_0), \tag{4.9}$$

where $K(T_0,P_0)$ is equilibrium constant dependent on total pressure $P_0 = kT{C^e}_{\text{tot}}$, temperature T_0 and naturally also the cluster size $\{N_{i,d}\}$.

To relate the equilibrium cluster distribution to the formation free energies derived earlier we need to express the chemical potentials in a hypothetical system, $\mu^{p,P_0}_{i,\text{mon}}$ and $\mu^{p,P_0}(\{N_{i,d}\})$, in terms of the properties of our mixture of clusters and monomers. Eq. (3.7) can be used to calculate the Gibbs free energy of a vapour consisting of only one type of monomers at pressure P_0 and temperature T_0

$$G = \mu_{i,g}(P_0, T_0)N_{i,g},$$

where $N_{i,g} = VC^e_{i,\mathrm{mon}}$ is the number of monomers in the system. The chemical potential of a monomer in this vapour is by definition (1.1)

$$\mu^{p,P_0}_{i,\mathrm{mon}} = \left(\frac{\partial G}{\partial N_{i,g}}\right)_{T_0,P_0} = \mu_{i,g}(P_0, T_0),$$

which is quite a natural result.

The Gibbs free energy of a system consisting of only $\{N_{i,d}\}$ clusters as a generalisation of eq. (3.8) is

$$G = N(\{N_{i,d}\})\left[(P_0 - P_l)V_l + \sigma A + \sum_i \mu_{i,l}N_{i,l} + \sum_i \mu_{i,s}N_{i,s}\right],$$

where $N(\{N_{i,d}\}) = VC^e(\{N_{i,d}\})$ is the number of clusters in the system, and $N_{i,d} = N_{i,l} + N_{i,s}$ is the number of component i molecules in each cluster. The chemical potential of a $\{N_{i,d}\}$ cluster in this vapour is

$$\begin{aligned}\mu^{p,P_0}(\{N_{i,d}\}) &= \left(\frac{\partial G}{\partial N(\{N_{i,d}\})}\right)_{T_0,P_0} \\ &=(P_0 - P_l)V_l + \sigma A + \sum_i \mu_{i,l}N_{i,l} + \sum_i \mu_{i,s}N_{i,s}.\end{aligned} \tag{4.10}$$

The combination of chemical potentials inside the exponential in the cluster distribution (4.8) can now be written in the following way

$$\begin{aligned}\mu^{p,P_0}(\{N_{i,d}\}) - \sum_i N_{i,d}\mu^{p,P_0}_{i,\mathrm{mon}} &= (P_0 - P_l)V_l + \sigma A \\ &+ \sum_i \mu_{i,l}N_{i,l} + \sum_i \mu_{i,s}N_{i,s} - \sum_i (N_{i,l} + N_{i,s})\mu_{i,g}(P_0, T_0) \\ &=(P_0 - P_l)V_l + \sigma A + \sum_i \left[\mu_{i,l} - \mu_{i,g}(P_0, T_0)\right] N_{i,l} \\ &+ \sum_i \left[\mu_{i,s} - \mu_{i,g}(P_0, T_0)\right] N_{i,s}.\end{aligned} \tag{4.11}$$

This expression is almost equal to the formation free $\Delta\varphi$ energy given for example as a change in grand potential when droplet forms($\Delta\Omega$) by eq. (3.6). The only difference is that in eq. (3.6) for the formation free energy we have the chemical potential of the vapour at partial pressure of the corresponding monomer vapour (denoted as $\mu^0_{i,g} = \mu_{i,g}(P_i, T_0)$, where $P_i = kTC^e_{i,\mathrm{mon}}$), and here we have the chemical potentials of the vapour at the pressure $P_0 = kTC^e{}_{\mathrm{tot}}$.

We convert the chemical potentials from pressure P_0 to the partial pressures of monomers using the ideal gas results (2.21)

$$\mu_{i,g}(P_0,T_0) = \mu_{i,g}(P_i,T_0) + kT \ln \frac{P_0}{P_i} = \mu^0_{i,g} + kT \ln \frac{{C^e}_{\text{tot}}}{C^e_{i,\text{mon}}}. \tag{4.12}$$

By inserting result (4.12) to expression (4.11) and using $N_{i,d} = N_{i,l} + N_{i,s}$ we get

$$\begin{aligned}
\mu^{p,P_0}(\{N_{i,d}\}) - \sum_i N_{i,d}\mu^{p,P_0}_{i,\text{mon}} &= (P_0 - P_l)V_l + \sigma A \\
&+ \sum_i \left[\mu_{i,l} - \mu^0_{i,g}\right] N_{i,l} + \sum_i \left[\mu_{i,s} - \mu^0_{i,g}\right] N_{i,s} - kT \sum_i N_{i,d} \ln \frac{{C^e}_{\text{tot}}}{C^e_{i,\text{mon}}} \\
&= \Delta\varphi - kT \sum_i \ln \left(\frac{{C^e}_{\text{tot}}}{C^e_{i,\text{mon}}}\right)^{N_{i,d}} .
\end{aligned} \tag{4.13}$$

The cluster distribution can now be written as

$$\begin{aligned}
C^e(\{N_{i,d}\}) &= {C^e}_{\text{tot}} \left(\frac{C^e_{1,\text{mon}}}{{C^e}_{\text{tot}}}\right)^{N_{1,d}} \cdots \left(\frac{C^e_{i,\text{mon}}}{{C^e}_{\text{tot}}}\right)^{N_{i,d}} \cdots \left(\frac{C^e_{n,\text{mon}}}{{C^e}_{\text{tot}}}\right)^{N_{n,d}} \\
&\cdot \exp\left\{-\frac{1}{kT}\left[\Delta\varphi - kT \sum_i \ln \left(\frac{{C^e}_{\text{tot}}}{C^e_{i,\text{mon}}}\right)^{N_{i,d}}\right]\right\} \\
&= {C^e}_{\text{tot}} \prod_i \left(\frac{C^e_{i,\text{mon}}}{{C^e}_{\text{tot}}}\right)^{N_{i,d}} \exp\left(\frac{-\Delta\varphi}{kT}\right) \exp\left[\ln \prod_i \left(\frac{{C^e}_{\text{tot}}}{C^e_{i,\text{mon}}}\right)^{N_{i,d}}\right],
\end{aligned}$$

where the latter exponent cancels the logarithm inside it; after that the products $\prod_i \left(\frac{C^e_{i,\text{mon}}}{{C^e}_{\text{tot}}}\right)^{N_{i,d}}$ and $\prod_i \left(\frac{{C^e}_{\text{tot}}}{C^e_{i,\text{mon}}}\right)^{N_{i,d}}$ cancel, and we get the equilibrium cluster distribution in terms of the formation free energy of the cluster

$$\boxed{C^e(\{N_{i,d}\}) = F^e \exp\left(\frac{-\Delta\varphi(\{N_{i,d}\})}{kT}\right),} \tag{4.14}$$

where we have denoted the cluster size independent pre-factor (of the exponential) by $F^e = {C^e}_{\text{tot}}$.

Some remarks on the equilibrium distribution:

- In principle results (4.8) and (4.14) are only applicable to true equilibrium situations, for example a vapour in equilibrium with some liquid. Sometimes it has been applied to so-called supersaturated equilibrium, meaning a nucleating vapour that is necessarily supersaturated with respect to the liquid having critical cluster composition. This liquid is thought to be forced to equilibrium with some extra force field similar to that discussed on p. 65. In eq. (4.14) $\Delta\varphi(\{N_{i,d}\})$ is then the formation energy of a cluster in the vapour in question, and $C^e_{\mathrm{tot}} = P_0/(kT)$ is the total number of clusters in the same vapour. In this book we use cluster distributions (4.8) and (4.14) only for true equilibrium vapour, which is a thermodynamically more sound approach.

- We have derived the equilibrium cluster distribution relying on the assumption that the mixture of clusters is an ideal mixture of ideal gases. If we also assume the liquid state to be incompressible we have according to eq. (3.30)
$$\Delta\varphi(\{N_{i,d}\}) = -kT\sum_i \ln\frac{\mathcal{A}_{i,g}}{\mathcal{A}_{i,l}(x_{i,l})} + \sigma A.$$
As shown on p. 99 this means that the distribution (4.14) can be written in the form (4.9), with gas phase activities $\mathcal{A}_{i,g} \propto C_{i,\mathrm{mon}}$ carrying the monomer concentration dependencies.
- Most often monomers have much higher concentrations than any other clusters in the equilibrium vapour, and the pre-factor $F^e = {C^e}_{\mathrm{tot}}$ is approximated by the sum of monomer concentrations in the equilibrium vapour $\sum_i C^e_{i,\mathrm{mon}}$.
- Approximation $F^e = \sum_i C^e_{i,\mathrm{mon}}$ is often said to violate the mass action law (4.9), because it introduces explicit dependence of pre-factor F^e (or equilibrium constant $K(T_0, P_0)$) on monomer concentrations. However, it must be kept in mind that the equilibrium constant does depend on the total pressure P_0, and if monomers dominate the vapour, dependence on total pressure means dependence on total concentration of monomers, and there is no discrepancy.
- The form of the chemical potential of a cluster given by eq. (4.10) is not consistent with statistical mechanical considerations. This leads to the fact that the pre-factor $F^e = C^e_{\mathrm{tot}}$ is not a correct normalisation constant for the equilibrium cluster distribution (Abraham 1974; Lothe and Pound 1962), but an experimentally tested consensus for the correct pre-factor is not available to this date.
- The cluster size distribution (4.14) suffers from various self-consistency problems. In the one-component case the distribution does not give monomer concentration C_{mon} when applied to clusters consisting of only one molecule. This is due to the fact that the formation free energy given by eq. (3.29) does not reduce to zero for monomers, because the surface term of free energy does not vanish for a single molecule (see p. 74).

  In multicomponent systems we have the same problem of not getting consistent monomer concentrations from distribution (4.14). The problem is more severe since with $S_i \neq 1$ in addition to the surface term also the $\ln S$ terms of free energy also gives a non-zero contribution for monomers.

Furthermore, the multicomponent distribution should reduce to a one-component distribution at the limit where all gas phase activities but one are set to zero. Various artificial devices for ensuring both types of consistencies have been developed in the literature (Wilemski and Wyslouzil 1995; Wilemski 1995; Girshick and Chiu 1990). Some of these self-consistent versions involve using a cluster size dependent pre-factor F^e if the distribution is written in the form (4.14).

Problems

4.1. a) Plot the equilibrium cluster distributions $C^e(n)$ for pure water at T=280K and T=300K.
b) Derive an expression for the cluster distribution $C(n)$ in nucleating one-component steady-state vapour and plot this distribution in figure a) with S=5 and S=10 at T=280K and T=300K.

The saturation vapour pressure of water (T in Kelvin)
$P_e = \exp[77.34 - 7235.42/T - 8.2\ln(T) + 0.00571T]$ Pa.
Density of liquid water is
$\rho_l = (1049.572 - 0.1763T)$ kg/m^3.
Molar mass of water is 18.02 g/mol.
Surface tension of pure water is
$\sigma = (0.117 - 0.152 \cdot 10^{-3}T)$ N/m.

5

Nucleation kinetics

Now we leave the stationary picture of equilibrium thermodynamics and see how the clusters are formed and how they break up (Nowakovski and Ruckenstein 1991a,b; Wilcox and Bauer 1991).

Clusters grow when monomers collide with them. There are many more monomers than clusters in normal vapours, so collisions between two clusters are very rare compared to cluster-monomer collisions. Thus they can be neglected. We also assume that only single monomers leave the cluster at a time. The rate at which monomers of type i collide with $\{N_{i,d}\}$ clusters is given by the kinetic gas theory as $\beta_i(\{N_{i,d}\}) \cdot C(\{N_{i,d}\})$, where $C(\{N_{i,d}\})$ is the concentration of the clusters and the condensation coefficient $\beta_i(\{N_{i,d}\})$ is given by the kinetic gas theory (Friedlander 1977; Chapman and Cowling 1970):

$$\boxed{\begin{aligned}\beta_i(\{N_{i,d}\}) =& C_{i,\mathrm{mon}}\left(\frac{3}{4\pi}\right)^{1/6}\left(\frac{6kT_0}{m(\{N_{i,d}\})}+\frac{6kT_0}{m_i}\right)^{1/2}\\ &\cdot\left\{[V(\{N_{i,d}\})]^{1/3}+[v_{i,l}^p]^{1/3}\right\}^2 .\end{aligned} \qquad (5.1)}$$

Here $C_{i,\mathrm{mon}}$ is the concentration of type i monomers, $m(\{N_{i,d}\})$ and m_i are the masses of the cluster and the monomer, $V(\{N_{i,d}\})$ is the volume of the cluster assumed to be a spherical droplet (the volume is calculated using liquid density for the cluster core composition $x_{i,l}$) and $v_{i,l}^p$ is the volume of the monomer (calculated as the molecular volume in pure liquid i). β_i is calculated by studying how often molecules following the Maxwell-Boltzmann velocity distribution hit a surface of a moving sphere, whose velocity is also given by a Maxwell-Boltzmann distribution. If the cluster is much larger than a monomer, $m(\{N_{i,d}\}) >> m_i$ and $V(\{N_{i,d}\}) >> v_{i,l}^p$, we can neglect the $v_{i,l}^p$ and $1/m(\{N_{i,d}\})$ terms in (5.1) (which is equivalent of neglecting the fact that also the cluster moves), and the condensation coefficient takes the form

$$\beta_i(\{N_{i,d}\}) = C_{i,\mathrm{mon}} A(\{N_{i,d}\}) \sqrt{\frac{kT}{2\pi m_i}},$$

where $A(\{N_{i,d}\})$ is the area of a spherical cluster with radius $r = \left(\frac{3}{4\pi}\right)^{1/3} V(\{N_{i,d}\})^{1/3}$.

In this book we have included the monomer concentration in the condensation coefficient, and the number of clusters grown per unit time is given by $C(\{N_{i,d}\})\beta$. Another possibility is to define $\beta' = \beta / C_{i,\mathrm{mon}}$, which means that the number of clusters grown in a unit time is given by $\beta' C_{i,\mathrm{mon}} C(\{N_{i,d}\})$, which better shows the symmetry of the condensation rate with respect to the concentrations of the colliding parties. Using β' would make the notation longer, and in the interest of simplicity we use β in this book.

Clusters of size $\{N_{i,d}\}$ loose one molecule of type k with a rate $\gamma_k(\{N_{i,d}\}) \cdot C(\{N_{i,d}\})$, where $\gamma(\{N_{i,d}\})$ is the evaporation coefficient. See Fig. 5.1 for an illustration of the transitions between different cluster sizes in a two-component system.

We separate the number of molecules of type k arriving or leaving from all other types $j \neq k$ by writing $\{N_{i,d}\} \equiv \{N_{j,d}, N_{k,d}\}$ as illustrated in Fig. 5.2. The concentration of size $\{N_{j,d}, N_{k,d}\}$ clusters changes due to the following processes:

1. Smaller ones grow:
   $+\mathrm{d}\sum_k \beta_k(\{N_{j,d}, N_{k,d} - 1\}) \cdot C(\{N_{j,d}, N_{k,d} - 1\})$.
   A monomer of type k hits a cluster $\{N_{i,d}, N_{k,d} - 1\}$ which is otherwise like $\{N_{j,d}, N_{k,d}\}$, but one molecule of type k is missing
2. The clusters themselves grow by a monomer of any type k:
   $-\mathrm{d}\sum_k \beta_k(\{N_{j,d}, N_{k,d}\}) \cdot C(\{N_{j,d}, N_{k,d}\})$.
3. Larger ones break up:
   $+\mathrm{d}\sum_k \gamma_k(\{N_{j,d}, N_{k,d} + 1\}) \cdot C(\{N_{j,d}, N_{k,d} + 1\})$.
   A monomer of type k leaves a cluster $\{N_{j,d}, N_{k,d} + 1\}$ which is otherwise like $\{N_{i,d}, N_{k,d}\}$, except that is has one more molecule of type k.
4. The clusters themselves break up, a molecule of type k leaves:
   $-\mathrm{d}\sum_k \gamma_k(\{N_{j,d}, N_{k,d}\}) \cdot C(\{N_{j,d}, N_{k,d}\})$.

The *birth-death equation* tells how the concentration of clusters change with time:

$$\begin{aligned}\frac{dC(\{N_{j,d}, N_{k,d}\})}{dt} =& \mathrm{d}\sum_k \Big[\beta_k(\{N_{j,d}, N_{k,d} - 1\}) \cdot C(\{N_{j,d}, N_{k,d} - 1\}) \\ &- \beta(\{N_{j,d}, N_{k,d}\}) \cdot C(\{N_{j,d}, N_{k,d}\}) \\ &- \gamma_k(\{N_{j,d}, N_{k,d}\}) \cdot C(\{N_{j,d}\}) \\ &+ \gamma_k(\{N_{j,d}, N_{k,d} + 1\}) \cdot C(\{N_{j,d}, N_{k,d} + 1\})\Big].\end{aligned} \tag{5.2}$$

We define the flow of the clusters for size $\{N_{i,d}\}$ in direction k as

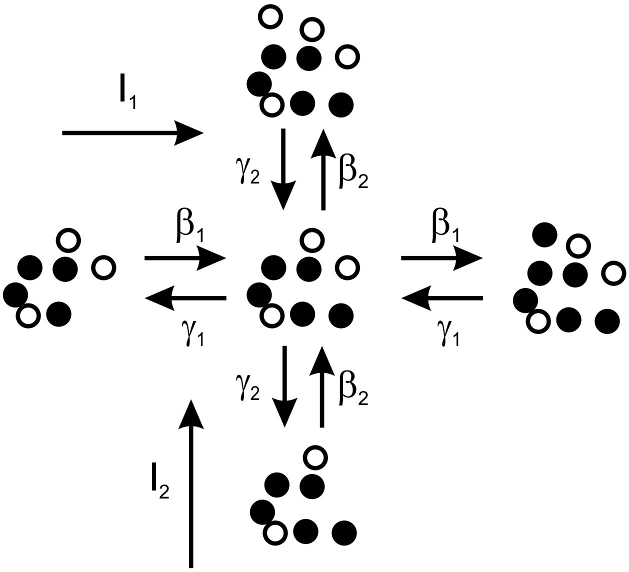


Fig. 5.1. Evaporation and condensation flows between adjacent cluster sizes in a two-component system. β_i is the condensation coefficient and γ_i is the evaporation coefficient for component $i = 1, 2$. Both the evaporation and condensation coefficients are dependent on the cluster size and composition, but the arguments indicating this dependency have been left out from the symbols in this figure for simplicity.

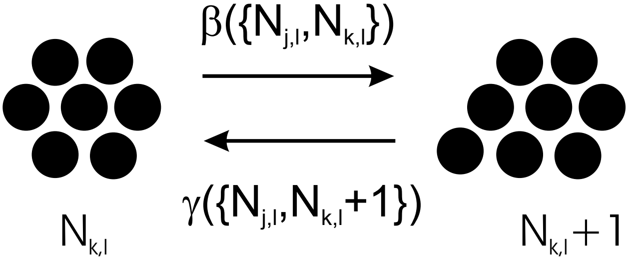


Fig. 5.2. Flows between two cluster sizes in the direction of the component k. $\beta_k^e(\{N_{j,d}, N_{k,d}\})$ is the rate at which molecules of type k hit the cluster with $N_{k,d}$ molecules of type k. The number of molecules $N_{j,d}$ of all types $j \neq k$ stay constant. The cluster formed in this process is denoted $\{N_{j,d}, N_{k,d} + 1\}$, it has one molecule of type k more than the original cluster. The rate at which these clusters break up by emitting one molecule of type k is $\gamma_k(\{N_{j,d}, N_{k,d} + 1\})$.

$$\begin{aligned} I_k(\{N_{j,d}, N_{k,d}\}) = &\beta_k(\{N_{j,d}, N_{k,d}\}) \cdot C(\{N_{j,d}, N_{k,d}\}) \\ &- \gamma_k(\{N_{j,d}, N_{k,d} + 1\}) \cdot C(\{N_{j,d}, N_{k,d} + 1\}). \end{aligned} \tag{5.3}$$

With this definition the birth-death equation takes a simple form

$$\boxed{\frac{dC(\{N_{j,d},N_{k,d}\})}{dt} = \mathrm{d}\sum_k I_k(\{N_{k,d},N_{k,d}-1\}) - I_k(\{N_{i,d},N_{k,d}\}). \qquad (5.4)}$$

We can solve the evolution of cluster concentrations $C(\{N_{i,d}\})$ from the set of birth-death equations (5.2) if we know the evaporation coefficients γ_k. This is the point where we once more have to turn back to equilibrium considerations. In the equilibrium vapour the concentrations of clusters stay constant:

$$C(\{N_{i,d}\}) = C^e(\{N_{i,d}\}) = \text{constant in time}, \qquad \frac{dC^e(\{N_{i,d}\})}{dt} = 0.$$

Nothing flows in the system either, $I_k(\{N_{i,d},N_{k,d}\}) = 0$, which means we have to have *detailed balance*: the rate of each process is equal to the rate of its counter-process.

$$\gamma_k(\{N_{j,d},N_{k,d}{+}1\})\cdot C^e(\{N_{j,d},N_{k,d}{+}1\}) = \beta_k^e(\{N_{j,d},N_{k,d}\})\cdot C^e(\{N_{j,d},N_{k,d}\}). \tag{5.5}$$

We assume that the probabilities of clusters to break up, in other words the evaporation coefficients, are independent of the vapour where the clusters are: We can calculate the evaporation coefficients in the true equilibrium vapour from

$$\boxed{\gamma_k(\{N_{j,d},N_{k,d}+1\}) = \beta_k^e(\{N_{j,d},N_{k,d}\})\frac{C^e(\{N_{j,d},N_{k,d}\})}{C^e(\{N_{j,d},N_{k,d+1}\})}. \qquad (5.6)}$$

NOTE 1: The condensation coefficient is calculated for the equilibrium vapour, so through β_k^e *it is proportional to the equilibrium concentration of monomers* $C^e_{\mathrm{mon},k}$*, not the monomer concentration in the studied, nucleating vapour. For multicomponent systems we can use the equilibrium vapour over a liquid of any composition to calculate the evaporation coefficients. The reference liquid composition cancels in our calculations (see p. 99).*

NOTE 2: Often especially in older literature the equilibrium constants are calculated in a hypothetical supersaturated equilibrium vapour, see p. 83.

The evaporation coefficients can also be calculated from the equality of condensation rate and evaporation rate for a single spherical droplet which is in equilibrium with the surrounding vapour. The pressure of this vapour is the saturation vapour pressure over a flat surface of the solution times the Kelvin factor $\exp[2\sigma v_{i,l}/(rkT)]$. With the approximation $A(\{N_{j,d},N_{k,d}{+}1\}) - A(\{N_{j,d},N_{k,d}\}) = \frac{\partial A}{\partial N_{k,d}}$ the result is the same as obtained from eq. (5.6).

We will now study nucleation in a supersaturated *steady-state* vapour, where the concentrations of all clusters stay constant $dC(\{N_{i,d}\})/dt = 0$, but in contrast to the equilibrium situation there is a flow of molecules through the system and the detailed balance is not valid. We assume that the vapour always behaves like an ideal gas, and thus concentrations are directly proportional to pressures.

5.1 One-component steady-state nucleation

In a one-component system $k = 1$ always, so component index k is not needed in the following. Denote $\{N_{i,d}\} \equiv n$, $C(\{N_{i,d}\}) \equiv C(n)$ and so on, with n as the number of molecules in the cluster. The monomer concentration is $C_{\mathrm{mon}} = C(1) = SP_e^p(T_0)/(kT_0)$ and the saturation ratio must be greater than one for nucleation to occur, $S = C(1)/C^e(1) > 1$.

The net flow to size n (eq. 5.3) simplifies to

$$I(n) = \beta(n)C(n) - \gamma(n+1)C(n+1).$$

The flow $I(n)$ gives the net flow of n molecule clusters (n-mers) to $n+1$ molecule clusters taking into account both growth from n to $n+1$ and decay from $n+1$ to n .

The birth-death equation (5.2) takes the form

$$\begin{aligned}\frac{dC(n)}{dt} =& \beta(n-1)C(n-1) - \beta(n)C(n) - \gamma(n)C(n) + \gamma(n+1)C(n+1) \\ =& I(n-1) - I(n).\end{aligned}$$

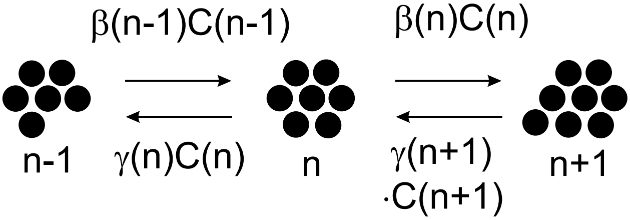


Fig. 5.3. Evaporation and condensation flows between sizes $n-1$, n and $n+1$ in a one-component system. $\beta(n)$ is the condensation coefficient and $\gamma(n)$ is the condensation coefficient for size n.

In a steady state the cluster concentrations do not change $\frac{dC(n)}{dt} = 0$, which implies that the flow of molecules from size $(n-1)$ to size n is independent of n, $I(n-1) = I(n) = I$. We want to calculate the formation rate of critical clusters, the *nucleation rate* J, which is thus equal to I. Now $\beta(n)C(n) \neq \gamma(n+1)C(n+1)$ and there is a flow through the system. In the steady state all the cluster concentrations and the monomer concentrations stay constant. This requires a continuous monomer source, or we have to assume that clusters are so rare compared to the monomers that their formation does not significantly lower the monomer concentration.

NOTE: In equilibrium $I^e(n) = 0$ for each n.

Using a detailed balance (5.5) to calculate evaporation coefficients as in eq. (5.6) we get

$$\gamma(n+1) = \beta^e(n)\frac{C^e(n)}{C^e(n+1)}$$

and the flow is

$$\begin{aligned} I &= \beta(n)C(n) - \beta^e(n)C^e(n)\frac{C(n+1)}{C^e(n+1)} \\ &= \beta^e(n)C^e(n)\left(\frac{\beta(n)}{\beta^e(n)}\frac{C(n)}{C^e(n)} - \frac{C(n+1)}{C^e(n+1)}\right). \end{aligned}$$

The condensation coefficient $\beta(n)$ is proportional to the pressure of the nucleating vapour, $\beta(n) \propto SP_s$, and $\beta^e(n)$ is proportional to the pressure of the equilibrium vapour, $\beta^e(n) \propto P_s$, and thus $\beta(n)/\beta^e(n) = S$. Using this and inserting S^{n+1} to the nominator and denominator at the second stage we obtain

$$\begin{aligned} I &= \beta^e(n)C^e(n)\left(S\frac{C(n)}{C^e(n)} - \frac{C(n+1)}{C^e(n+1)}\right) \\ &= \beta^e(n)C^e(n)S^{n+1}\left(\frac{C(n)}{C^e(n)S^n} - \frac{C(n+1)}{C^e(n+1)S^{n+1}}\right) \\ &= \underbrace{S\beta^e(n)}_{\beta(n)}C^e(n)S^n\left(\frac{C(n)}{C^e(n)S^n} - \frac{C(n+1)}{C^e(n+1)S^{n+1}}\right) \\ I &= \beta(n)C^e(n)S^n\left(\frac{C(n)}{C^e(n)S^n} - \frac{C(n+1)}{C^e(n+1)S^{n+1}}\right). \end{aligned}$$

This equation can be rearranged to give

$$\frac{I}{\beta(n)C^e(n)S^n} = \frac{C(n)}{C^e(n)S^n} - \frac{C(n+1)}{C^e(n+1)S^{n+1}}. \tag{5.7}$$

We sum up equations (5.7) with $n = 1, \ldots, \mathcal{N}$ where $\mathcal{N}$ is so far any arbitrary number > 2.

$$\begin{aligned} \frac{I}{\beta(1)C^e(1)S} &= \frac{C(1)}{C^e(1)S^1} - \frac{C(2)}{C^e(2)S^2} \\ \frac{I}{\beta(2)C^e(2)S^2} &= \frac{C(2)}{C^e(2)S^2} - \frac{C(3)}{C^e(3)S^3} \\ &\vdots \\ \frac{I}{\beta(\mathcal{N})C^e(\mathcal{N})S^{\mathcal{N}}} &= \frac{C(\mathcal{N})}{C^e(\mathcal{N})S^{\mathcal{N}}} - \frac{C(\mathcal{N}+1)}{C^e(\mathcal{N}+1)S^{\mathcal{N}+1}}. \end{aligned}$$

The last term on the right-hand side of each equation is cancelled by the first term on the right-hand side of the next equation and we get

$$I\sum_{n=1}^{\mathcal{N}}\frac{1}{\beta(n)C^e(n)S^n}=\frac{C(1)}{C^e(1)S}-\frac{C(\mathcal{N}+1)}{C^e(\mathcal{N}+1)S^{\mathcal{N}+1}}. \tag{5.8}$$

The monomer concentration ($\propto$ pressure) is related to the saturation ratio and equilibrium monomer concentration ($\propto$ saturation vapour pressure), $C(1)=C^e(1)S$, which means that the first term on the right-hand side of eq. (5.8) equals 1. If we take $\mathcal{N}$ to infinity and assume

$$\frac{C(\mathcal{N}+1)}{C^e(\mathcal{N}+1)S^{\mathcal{N}+1}}\rightarrow 0 \text{ for } \mathcal{N}\rightarrow\infty, \tag{5.9}$$

then eq. (5.8) reduces to

$$I\sum_{n=1}^{\infty}\frac{1}{\beta(n)C^e(n)S^n}=1-0=1,$$

from which we can solve the flow I which is equal to the nucleation rate J

$$\boxed{J=I=\left[\sum_{n=1}^{\infty}\left(\frac{1}{\beta(n)C^e(n)S^n}\right)\right]^{-1}. \qquad (5.10)}$$

The sum in eq. (5.10) can be calculated accurately to get the nucleation rate, but more often people go to the continuum limit and calculate the sum as an integral

$$I^{-1}=\sum_{n=1}^{\infty}\frac{1}{\beta(n)C^e(n)S^n}\approx\int_1^{\infty}\frac{1}{\beta(n)C^e(n)S^n}dn. \tag{5.11}$$

One could make the continuum approximation in differential form already earlier in eq. (5.7) and arrive at the same integral by writing

$$\frac{I}{\beta(n)C^e(n)S^n}=-\frac{\partial}{\partial n}\left(\frac{C(n)}{C^e(n)S^n}\right),$$

the integral of which gives

$$\int_1^{\infty}\frac{Idn}{\beta(n)C^e(n)S^n}=-\bigg/_{\!1}^{\infty}\frac{C(n)}{C^e(n)S^n}=1.$$

The last equality follows since $C(1)=C^e(1)S$ and we assume that

$$\lim_{n\rightarrow\infty}\frac{C(n)}{C^e(n)S^n}=0.$$

To calculate the integral we recall the form of the equilibrium cluster distribution (4.14)

$$C^e(n) = F^e \exp\left(- \frac{\Delta\varphi^e(n)}{kT_0} \right).$$

Remember that we are using the equilibrium distribution in the true equilibrium vapour and specify this choice by adding the superscript ^{e} to the formation free energy. The denominator of the integrand in eq. (5.11) can be written as

$$C^e(n) \cdot S^n = F^e \cdot \exp\left(\frac{-\Delta\varphi^e(n) + kT_0 n \ln S}{kT_0} \right), \tag{5.12}$$

where

$$\Delta\varphi^e(n) = n\Delta\mu^e + A\sigma,$$

but for one-component equilibrium vapour $S = 1$ and thus $\Delta\mu^e = kT_0 \ln S = 0$ and the function inside the exponential in eq. (5.12) can be written as

$$\frac{1}{kT_0}\left(-\Delta\varphi^e(n) + kT_0 n \ln S\right) = \frac{1}{kT_0}\left(-A\sigma + kT_0 n \ln S\right) = -\Delta\varphi(n))$$

which is the formation energy in the supersaturated vapour (for ideal gas $\Delta\mu = kT_0 \ln S$ in one-component system).

The integral (5.11) can now be written as

$$I^{-1} = \int_1^\infty dn \frac{1}{\beta(n) C^e(n) S^n} = \int_1^\infty \frac{1}{\beta(n)} \frac{1}{F^e} \exp\left(\frac{\Delta\varphi(n)}{kT_0} \right).$$

The behaviour of $\frac{\Delta\varphi(n)}{kT_0}$ and $\exp\left(\frac{\Delta\varphi(n)}{kT_0}\right)$ as functions of n are sketched in Fig. 5.4, both of them have a maximum at the critical size, but the maximum of $\exp\left(\frac{\Delta\varphi(n)}{kT_0}\right)$ is much sharper.

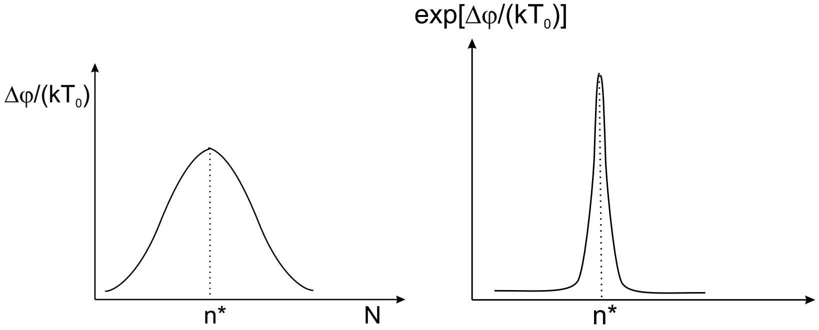


Fig. 5.4. $\frac{\Delta\varphi(n)}{kT_0}$ and $\exp\left(\frac{\Delta\varphi(n)}{kT_0}\right)$ as a function of number of molecules in the cluster n.

The maximum of the exponential is so sharp that only the region around the critical size contributes to the integral. Inside the integral we will thus approximate

$$\beta(n) \approx \beta(n^*)$$

and use (see p. 83)

$$F^e = C^e(1) + \sum_{n=2}^{\infty} C^e(n) \approx C^e(1)$$

assuming there are many more monomers than clusters in the equilibrium vapour. We can also expand $\Delta\varphi$ as a Taylor series around n^*:

$$\Delta\varphi(n) = \Delta\varphi(n^*) + \left(\frac{\partial \Delta\varphi}{\partial n}\right)_{n^*} (n - n^*) + \frac{1}{2}\left(\frac{\partial^2 \Delta\varphi}{\partial n^2}\right)_{n^*} (n - n^*)^2 + \cdots$$

Because $\Delta\varphi$ has a maximum at n^*, the first derivative is zero

$$\left(\frac{\partial \Delta\varphi}{\partial n}\right)_{n^*} = 0$$

and the second derivative denoted by W^* is negative

$$-W^* \equiv \left(\frac{\partial^2 \Delta\varphi}{\partial n^2}\right)_{n^*} < 0.$$

With these assumptions and definitions the integral (5.11) becomes

$$\begin{aligned} I^{-1} &= \frac{1}{\beta(n^*)C^e(1)} \int_1^{\infty} \exp\left(\frac{\Delta\varphi^*}{kT_0} + \frac{1}{2}\frac{-W^*}{kT_0}(n - n^2)^2\right) dn \\ &= \frac{\exp(\frac{\Delta\varphi^*}{kT_0})}{\beta(n^*)C^e(1)} \int_{-\infty}^{\infty} \exp\left(\frac{-W^*}{2kT_0}x^2\right) dx, \end{aligned}$$

where we have changed the integration variable to $x = n - n^*$ and treated the integration limits loosely: the integrand is almost zero for very low n and very high n, so we can replace the lower limit with $-\infty$. Starting this integral from $x = 0$ instead of $-\infty$ would leave out half of the most important region around the critical size, and is thus erroneous, but is sometimes done in the literature.

Now from an integral table (or with residy tricks)

$$\int_{-\infty}^{\infty} \exp\left(- az^2\right) dz = \sqrt{\frac{\pi}{a}}$$

and we can evaluate the integral

$$\int_{-\infty}^{\infty} \exp\left(\frac{-W^*}{2kT_0}x^2\right) dx = \sqrt{\frac{2\pi kT_0}{W^*}},$$

which gives

$$I^{-1} = \frac{\exp(\frac{\Delta\varphi^*}{kT_0})}{\beta(n^*)C^e(1)}\sqrt{\frac{2\pi kT_0}{W^*}}.$$

The nucleation rate is finally

$$\boxed{J = I = \beta(n^*)C^e(1)\exp(\frac{-\Delta\varphi^*}{kT_0})Z, \qquad (5.13)}$$

where

$$Z \equiv \sqrt{\frac{W^*}{2\pi kT_0}}$$

is called the *Zeldovich non-equilibrium factor*, which we will now calculate.

We need the second derivative of the formation free energy with respect to the number of molecules in the cluster taken at the critical size n^*. To make the derivation easier the formation free energy is first expressed in terms of the radius r instead of n using $nv_l = 4/3\pi r^3$ and $A = 4\pi r^2$.

$$\Delta\varphi = n\Delta\mu + \sigma A = \frac{4}{3}\pi r^3\frac{\Delta\mu}{v_l} + 4\pi r^2\sigma. \qquad (5.14)$$

We also need the derivative of radius with respect to number of molecules in the cluster $\frac{\partial n}{\partial r} = 4\pi r^2/v_l \Leftrightarrow \frac{\partial r}{\partial n} = v_l/(4\pi r^2)$

NOTE: The partial derivatives behave like normal derivatives since r only depends on n and there are no other variables involved. In a one-component system, taking the derivatives is generally easy since v_l, σ and $\Delta\mu$ are constants. This is because composition (and temperature) is unchanged.

The first derivative of the formation free energy is

$$\frac{\partial\Delta\varphi}{\partial n} = \frac{\partial\Delta\varphi}{\partial r}\frac{\partial r}{\partial n} = \left(\frac{\Delta\mu}{v_l}4\pi r^2 + 8\pi r\sigma\right)\frac{v_l}{4\pi r^2} = \Delta\mu + \frac{2v_l\sigma}{r}.$$

This is a familiar result, actually the left-hand side of the Kelvin eq. (2.15), and the previous derivation shows how to arrive at the Kelvin equation by finding the extrema of the formation free energy in a one-component system with a radius-independent surface tension. We have to take the second derivative for the Zeldovich factor

$$-W^* = \left(\frac{\partial^2\Delta\varphi}{\partial n^2}\right)_* = \frac{\partial\left(\Delta\mu + \frac{2v_l\sigma}{r}\right)}{\partial r}\frac{\partial r}{\partial n}|_* = \frac{-2v_l\sigma}{r^{*2}}\frac{v_l}{4\pi r^2} = \frac{-v_l^2\sigma}{2\pi r^{*4}}.$$

The Zeldovich factor becomes

$$Z = \sqrt{\frac{W^*}{2\pi kT_0}} = \sqrt{\frac{\sigma}{kT_0}\frac{v_l}{2\pi r^{*2}}}. \tag{5.15}$$

We would have arrived at this neat form with more cumbersome manipulations if we had expressed the area A in eq. (5.14) in terms of n and taken all the derivatives directly with respect to n.

Summary of predicting one-component nucleation rate

To get the nucleation rate we have to

1. Calculate the critical cluster radius r^* from eq. (2.24), which for a one-component system reduces to

$$r = \frac{2\sigma v_l}{-\Delta\mu} = \frac{2\sigma v_l}{kT\ln S}. \tag{5.16}$$

   Composition does not need to be solved, there are no options for it.
2. Calculate the formation free energy for the critical cluster, or in other words, the nucleation barrier height, given by eq. (3.9)

$$\Delta\varphi^* = -kT_0 n^* \ln S + A^*\sigma^* = \frac{4}{3}\pi\sigma r^{*2}.$$

3. Calculate the condensation coefficient $\beta(n^*)$ from eq. (5.1) which for a one component system with $C_{\text{mon}} = SP_e^p(T_0)/(kT_0)$ takes the form

$$\beta(n^*) = SP_e^p(T_0)\sqrt{\frac{6}{kT_0}}\big(\frac{3}{4\pi}\big)^{1/6}\big(\frac{1}{n^* m_1} + \frac{1}{m_1}\big)^{1/2}\big(v^{*1/3} + v_l^{1/3}\big)^2,$$

   where m_1 is the mass of molecule of the nucleating vapour and v_l is the molecular volume in the bulk liquid and we have used the ideal gas assumption for the monomer concentration $C_{\text{mon}} = C(1) = SP_e^p(T_0)/(kT_0)$.
4. Calculate the nucleation rate itself from equation

$$\boxed{J = \beta(n^*)C^e(1)\exp\big(-\frac{\Delta\varphi^*}{kT_0}\big)\sqrt{\frac{\sigma}{kT_0}\frac{v_l}{2\pi r^{*2}}}.} \tag{5.17}$$

Nucleation rate is often written as a product of three terms:

$$J = \beta(n^*)\cdot C^*\cdot Z = \beta(n^*)\cdot C_1^e\cdot\exp\big(\frac{-\Delta\varphi^*}{kT_0}\big)\cdot Z, \tag{5.18}$$

where $C^* = C_1^e\exp\big(\frac{-\Delta\varphi^*}{kT_0}\big)$. C^* is *not* the equilibrium concentration of size n^* clusters, because $\Delta\varphi^*$ is calculated in the supersaturated vapour.

$$C^* = C_1^e \exp\left(\frac{-\Delta\varphi^*}{kT_0}\right) = C_1^e \exp\left(\frac{-\Delta\varphi^e(n^*)}{kT_0}\right) S^{n*} = C^e(n^*) S^{n*}$$

$C^e(n^*)$ is the concentration of n^* clusters in the equilibrium vapour. So C^* is not really a concentration of n^* sized clusters in *any* vapour. However, C^* is the most important term since it contains the nucleation barrier height $\Delta\varphi^*$. The higher the barrier, the lower the nucleation rate, and dependence of the rate on the barrier height is strong because $\Delta\varphi^*$ is in the exponent.

5.2 1/S factor

If we had used the equilibrium cluster distribution (4.14) in the hypothetical supersaturated vapour (instead of the true equilibrium vapour) to calculate the evaporation coefficients the expression for the nucleation rate would be

$$J_S = \beta(n^*) \cdot C_1(S) \cdot \exp\left(\frac{-\Delta\varphi^*}{kT_0}\right) \cdot Z = \beta(n^*) C^{eS}(n^*) Z, \tag{5.19}$$

where $C^{eS}(n^*)$ is the concentration of critical clusters in the hypothetical supersaturated equilibrium vapour. In this case the formula for the nucleation rate can be interpreted as follows: the nucleation rate is the growth rate of critical clusters $\beta(n^*)$ times the concentration of critical clusters in supersaturated equilibrium $C^{eS}(n^*)$, times the Zeldovich factor Z which accounts for the fact that nucleating vapour is not in equilibrium. The Zeldovich factor is often called the Zeldovich non-equilibrium factor. However, the Zeldovich factor can not be used to calculate steady-state cluster concentrations from equilibrium (hypothetical or true) concentrations. Z is a rather abstract result of an integral performed around the critical size region, and accounts, among other things, for the fact that clusters do not only move toward larger sizes at the critical size, but there is evaporation flow to smaller clusters as well.

The difference between the formula (5.17), (or equivalently eq. 5.18) and formula (5.19) is a factor $J/J_S = 1/S$. The $1/S$ factor arises also if we calculate evaporation coefficients using the equilibrium distribution (4.14) in the hypothetical supersaturated vapour and

- modify the pre-factor F^e to be the monomer concentration in the *saturated* vapour to avoid making F^e dependent on monomer concentrations, which would seemingly violate the mass action law (see p. 83).
- make the equilibrium cluster distribution in hypothetical supersaturated equilibrium self-consistent in the sense that the distribution gives the correct result for single monomers (see p. 84). $1/S$ factor in front of $C^e(n) = C_{\text{mon}} \exp[(-nkT \ln S + \sigma A)/kT]$ causes the $\ln S$-dependent part to behave consistently for monomers, but another factor is needed for the surface term.

Eq. (5.19) is the form of the nucleation rate originally derived using classical theory, and there has been a lot of debate about the $1/S$ factor in the literature (Courtney 1961; Weaklim and Reiss 1994; Blander and Katz 1972). In this book the $1/S$ version (5.17) is preferred due to the fact that true equilibrium is believed to be the only thermodynamically acceptable reference state for calculating the evaporation coefficients.

5.3 Two-component steady-state nucleation

In a two-component case we denote $\{N_{i,d}\} \equiv (i,j)$, $C(\{N_{i,d}\}) \equiv C(i,j)$ and so on. $C(i,j)$ is the concentration of clusters with i molecules of type 1 and j molecules of type 2. The birth-death equation has the form

$$\frac{dC(i-1,j)}{dt} = I_1(i-1,j) - I_1(i,j) + I_2(i,j-1) - I_2(i,j) \approx -\frac{\partial I_1}{\partial i} - \frac{\partial I_2}{\partial j},$$

where we have gone to the continuum limit. In two-component systems we define a vector operator $\nabla = (\frac{\partial}{\partial i}, \frac{\partial}{\partial j})$ and a net flow vector $\overline{I} = \begin{pmatrix} I_1 \\ I_2 \end{pmatrix}$. The birth-death equation at the continuum limit takes the form $\frac{dC(i,j)}{dt} = -\nabla \cdot \overline{I}$ and in the steady state we have $\frac{dC(i,j)}{dt} = 0 = -\nabla \cdot \overline{I}$

Outline for calculating the multicomponent nucleation rate

Now we would like to find out the magnitude and direction of the critical cluster flow in the (i,j)-plane. We will then assume that only the critical size region contributes to the integral and in that region the flow direction θ is constant.

In the (x,y)- coordinate system with x-axis parallel to the critical size flow the critical region flow then has the form

$$\overline{I}_{x,y} = \begin{pmatrix} I_x \\ 0 \end{pmatrix},$$

and the gradient of the flow in these coordinates gives

$$\nabla_{x,y} \cdot \overline{I}_{x,y} = \frac{\partial I_x}{\partial x} + \frac{\partial 0}{\partial y} = 0,$$

which tells that

$$\frac{\partial I_x}{\partial x} = 0.$$

So I_x can depend only on y, not on x

$$I_x = I_x(y),$$

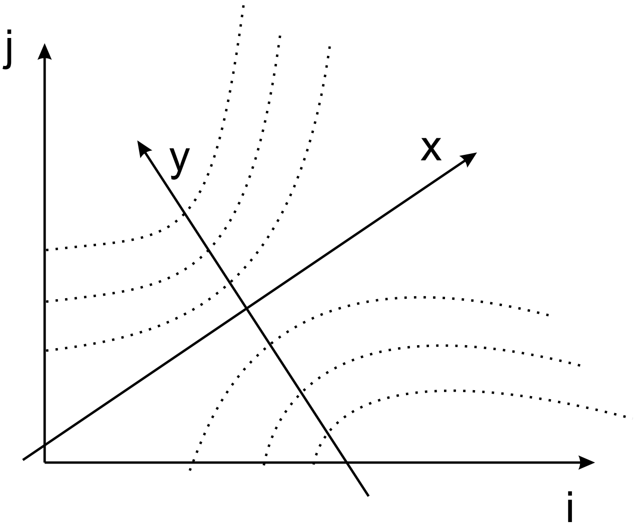


Fig. 5.5. Rotated coordinate system (x, y) with saddle point flow along the x-axis.

in other words I_x is constant along lines parallel to the x-axis (parallel to the critical size flow). We can integrate the flow along these lines, get I_x out of the integral and solve it just like in the one-component case. Then we can integrate $I_x(y)$ over different values of y and get the total flow passing the critical size region. We have to begin with finding an expression for $\vec{I}$ and a coordinate system where the flow has the form $\vec{I}_{x,y} = \begin{pmatrix} I_x \\ 0 \end{pmatrix}$ around the critical size.

The flow vector in two-component systems

Net flow in direction 1 is defined as

$$I_1(i,j) = \beta_1(i,j)C(i,j) - \gamma_1(i+1,j)C(i+1,j).$$

Using the detailed balance to eliminate the evaporation coefficients we get

$$\begin{aligned} I_1(i,j) &= \beta_1(i,j)C(i,j) - \beta_1^e(i,j)\frac{C^e(i,j)}{C^e(i+1,j)}C(i+1,j) \\ &= \beta_1^e(i,j)C^e(i,j)\left[\frac{\beta_1(i,j)C(i,j)}{\beta_1^e(i,j)C^e(i,j)} - \frac{C(i+1,j)}{C^e(i+1,j)}\right]. \end{aligned}$$

$\beta_1(i,j) \propto \mathcal{A}_{1,g}P_{1,e}^p(T_0)$, in other words the condensation coefficient β_1 is proportional to the vapour pressure of component 1 in the nucleating vapour, whereas the condensation coefficient β_1^e is proportional to the equilibrium vapour pressure over some reference liquid with composition x_l^e, $\beta_1^e(i,j) \propto \mathcal{A}_{1,l}(x_l^e)P_{1,e}^p(T_0)$.

Choice of the reference liquid

Now we show that we can choose any reference liquid x_l^e. In the equilibrium vapour over that liquid the gas phase activities are $\mathcal{A}_{1,g}^e = \mathcal{A}_{1,l}(x_l^e)$ and $\mathcal{A}_{2,g}^e = \mathcal{A}_{2,l}(x_l^e)$. We denote

$$\beta_1^e(i,j) = \mathcal{A}_{1,g}^e \beta_1^0(i,j),$$

where β_i^0 is the part which is independent of gas phase activities (see eq. 5.1)

$$\beta_i^0(i,j) = P_{i,e}^p(T_0)\sqrt{\frac{6}{kT_O}}\Big(\frac{3}{4\pi}\Big)^{1/6}\Big(\frac{1}{m(i,j)} + \frac{1}{m_1}\Big)^{1/2}\big(v(i,j)^{1/3} + v_1^{1/3}\big)^2.$$

The equilibrium cluster distribution is given by eq. (4.14)

$$C^e(i,j) = F^e \exp\Big(\frac{-\Delta\varphi^e(i,j)}{kT_0}\Big).$$

For an ideal gas mixture the formation energy of a cluster is

$$\Delta\varphi^e(i,j) = A\sigma - ikT_0 \ln\frac{\mathcal{A}_{1,g}^e}{\mathcal{A}_{1,l}(i,j)} - jkT_0 \ln\frac{\mathcal{A}_{2,g}^e}{\mathcal{A}_{2,l}(i,j)}$$

and the equilibrium distribution takes the form

$$\begin{aligned} C^e(i,j) &= F^e \exp\left(\frac{-A\sigma + ikT_0\ln\frac{\mathcal{A}_{1,g}^e}{\mathcal{A}_{1,l}(i,j)} + jkT_0\ln\frac{\mathcal{A}_{2,g}^e}{\mathcal{A}_{2,l}(i,j)}}{kT_0}\right) \\ &= F^e\left(\frac{\mathcal{A}_{1,g}^e}{\mathcal{A}_{1,l}(i,j)}\right)^i\left(\frac{\mathcal{A}_{2,g}^e}{\mathcal{A}_{2,l}(i,j)}\right)^j \exp\left(\frac{-A(i,j)\sigma(i,j)}{kT_0}\right). \end{aligned} \tag{5.20}$$

By replacing i with $i+1$ we get

$$\begin{aligned} C^e(i+1,j) =& F^e\left(\frac{\mathcal{A}_{1,g}^e}{\mathcal{A}_{1,l}(i+1,j)}\right)^{i+1}\left(\frac{\mathcal{A}_{2,g}^e}{\mathcal{A}_{2,l}(i,j)}\right)^j \\ &\cdot \exp\left(\frac{-A(i+1,j)\sigma(i+1,j)}{kT_0}\right). \end{aligned}$$

Now the evaporation coefficient can be calculated from the detailed balance (5.5)

$$\gamma_1(i,j) = \beta_1^e(i-1,j)\frac{C^e(i-1,j)}{C^e(i,j)}$$

and it reads

$$\begin{aligned} \gamma_1(i,j) =& \mathcal{A}_{1,g}^e \beta_1^0(i,j)\frac{F^e}{F^e}\frac{[\mathcal{A}_{1,l}(i+1,j)]^{i+1}}{\mathcal{A}_{1,g}^e[\mathcal{A}_{1,l}(i,l)]^i} \\ &\cdot \exp\left(\frac{A(i+1,j)\sigma(i+1,j) - A(i,j)\sigma(i,j)}{kT_0}\right), \end{aligned}$$

and we can derive a similar equation for $\gamma_2(i,j)$. We see that γ_1 and γ_2 are independent of the chosen equilibrium vapour used as a reference case since $\mathcal{A}_{1,g}^e$ (and $\mathcal{A}_{2,g}^e$) cancel.

Developing the formula for the flow vector

Using a reference liquid with $\mathcal{A}^e_{1,g}$ and $\mathcal{A}^e_{2,g}$ we get the expression for the net flow in the form

$$\begin{aligned}
I_1(i,j) =&\beta^e_1(i,j)C^e(i,j)\left(\frac{\mathcal{A}_{1,g}}{\mathcal{A}^e_{1,g}}\frac{C(i,j)}{C^e(i,j)} - \frac{C(i+1,j)}{C^e(i+1,j)}\right)\\
=&\beta^e_1(i,j)C^e(i,j)\left(\frac{\mathcal{A}_{1,g}}{\mathcal{A}^e_{1,g}}\right)^{i+1}\left(\frac{\mathcal{A}_{2,g}}{\mathcal{A}^e_{2,g}}\right)^{j}\\
&\cdot\left(\frac{C(i,j)}{C^e(i,j)\cdot(\mathcal{A}_{1,g}/\mathcal{A}^e_{1,g})^i\cdot(\mathcal{A}_{2,g}/\mathcal{A}^e_{2,g})^j}\right.\\
&\left. - \frac{C(i+1,j)}{C^e(i+1,j)\cdot(\mathcal{A}_{1,g}/\mathcal{A}^e_{1,g})^{i+1}\cdot(\mathcal{A}_{2,g}/\mathcal{A}^e_{2,g})^j}\right)\\
=&\beta_1(i,j)C^e(i,j)\left(\frac{\mathcal{A}_{1,g}}{\mathcal{A}^e_{1,g}}\right)^{i}\left(\frac{\mathcal{A}_{2,g}}{\mathcal{A}^e_{2,g}}\right)^{j}\\
&\cdot\left(\frac{C(i,j)}{C^e(i,j)\cdot(\mathcal{A}_{1,g}/\mathcal{A}^e_{1,g})^i\cdot(\mathcal{A}_{2,g}/\mathcal{A}^e_{2,g})^j}\right.\\
&\left. - \frac{C(i+1,j)}{C^e(i+1,j)\cdot(\mathcal{A}_{1,g}/\mathcal{A}^e_{1,g})^{i+1}\cdot(\mathcal{A}_{2,g}/\mathcal{A}^e_{2,g})^j}\right),
\end{aligned}$$

where we have multiplied both the nominator and the denominator with $\left(\mathcal{A}_{2,g}/\mathcal{A}^e_{2,g}\right)^j$ in anticipation of combining I_1 and I_2 to a single vector $\overline{I}$ and used $\beta_1/\beta^e_1 = \mathcal{A}_{1,g}/\mathcal{A}^e_{1,g}$. The cluster size distribution $C^e(i,j)$ above the reference liquids is given by eq. (5.20) and we get

$$C^e(i,j)\left(\frac{\mathcal{A}_{1,g}}{\mathcal{A}^e_{1,g}}\right)^{i}\left(\frac{\mathcal{A}_{2,g}}{\mathcal{A}^e_{2,g}}\right)^{j}$$

$$\begin{aligned}
=&F^e\exp\left(\frac{-A(i,j)\sigma(i,j + ikT_0\dfrac{\mathcal{A}^e_{1,g}}{\mathcal{A}_{1,l}(i,j)} + jkT_0\dfrac{\mathcal{A}^e_{2,g}}{\mathcal{A}_{2,l}(i,j)})}{kT_0}\right)\\
&\cdot\left(\frac{\mathcal{A}_{1,g}}{\mathcal{A}^e_{1,g}}\right)^{i}\left(\frac{\mathcal{A}_{2,g}}{\mathcal{A}^e_{2,g}}\right)^{j}\\
=&F^e\left(\frac{\mathcal{A}^e_{1,g}}{\mathcal{A}_{1,l}(i,j)}\right)^{i}\left(\frac{\mathcal{A}^e_{2,g}}{\mathcal{A}_{2,l}(i,j)}\right)^{j}\exp\left(\frac{-A(i,j)\sigma(i,j)}{kT_0}\right)\left(\frac{\mathcal{A}_{1,g}}{\mathcal{A}^e_{1,g}}\right)^{i}\left(\frac{\mathcal{A}_{2,g}}{\mathcal{A}^e_{2,g}}\right)^{j}\\
=&F^e\exp\left(\frac{-A\sigma + ikT_0\ln\frac{\mathcal{A}_{1,g}}{\mathcal{A}_{1,l}(x)} + jkT_0\ln\frac{\mathcal{A}_{2,g}}{\mathcal{A}_{2,l}(x)}}{kT_0}\right) = F^e\exp\left(\frac{-\Delta\varphi(i,j)}{kT_0}\right),
\end{aligned}$$

where energy $\Delta\varphi(i,j)$ is the formation energy of the (i,j) cluster in the nucleating vapour with gas phase activities $\mathcal{A}_{1,g}$ and $\mathcal{A}_{2,g}$. At the continuum limit the flow in direction of component 1 is

$$\begin{aligned}I_1(i,j) =&\beta_1(i,j)C^e(i,j)\left(\frac{\mathcal{A}_{1,g}}{\mathcal{A}^e_{1,l}}\right)^i\left(\frac{\mathcal{A}_{2,g}}{\mathcal{A}^e_{2,l}}\right)^j\\ &\cdot\left(-\frac{\partial}{\partial i}\left(\frac{C(i,j)}{C^e(i,j)\left(\frac{\mathcal{A}_{1,g}}{\mathcal{A}^e_{1,l}}\right)^i\left(\frac{\mathcal{A}_{2,g}}{\mathcal{A}^e_{2,l}}\right)^j}\right)\right)\\ =&\beta_1(i,j)F^e\exp\left(\frac{-\Delta\varphi(i,j)}{kT_0}\right)\cdot\left(-\frac{\partial}{\partial i}\left(\frac{C(i,j)}{F^e\exp\left(\frac{-\Delta\varphi(i,j)}{kT_0}\right)}\right)\right),\end{aligned}$$

and similarly the flow in direction of component 2 is

$$\begin{aligned}I_2(i,j) =&\beta_2(i,j)C^e(i,j)\left(\frac{\mathcal{A}_{1,g}}{\mathcal{A}^e_{1,l}}\right)^i\left(\frac{\mathcal{A}_{2,g}}{\mathcal{A}^e_{2,l}}\right)^j\\ &\cdot\left(-\frac{\partial}{\partial j}\left(\frac{C(i,j)}{C^e(i,j)\left(\frac{\mathcal{A}_{1,g}}{\mathcal{A}^e_{1,l}}\right)^i\left(\frac{\mathcal{A}_{2,g}}{\mathcal{A}^e_{2,l}}\right)^j}\right)\right)\\ =&\beta_2(i,j)F^e\exp\left(\frac{-\Delta\varphi(i,j)}{kT_0}\right)\cdot\left(-\frac{\partial}{\partial j}\left(\frac{C(i,j)}{F^e\exp\left(\frac{-\Delta\varphi(i,j)}{kT_0}\right)}\right)\right).\end{aligned}$$

We construct a vector $\overline{I} = \begin{pmatrix} I_1 \\ I_2 \end{pmatrix}$ describing the flow of clusters in all directions (Binder and Stauffer 1976)

$$\overline{I} = -\underline{R}F^e\exp\left(\frac{-\Delta\varphi(i,j)}{kT_0}\right)\nabla\left(\frac{C}{F^e\exp\left[\frac{-\Delta\varphi(i,j)}{kT_0}\right]}\right),$$

where the growth matrix $\underline{R}$ is defined as

$$\underline{R} = \begin{pmatrix} \beta_1(i,j) & \beta_{1,2}(i,j) \\ \beta_{1,2}(i,j) & \beta_2(i,j) \end{pmatrix}.$$

The off-diagonal elements of $\underline{R}$ ($\beta_{1,2}$) are equal to zero in this case, but they can also be non-zero if we take cluster-cluster collisions and cluster “fissions” into two daughter clusters (both larger than a monomer) into account

(Binder and Stauffer 1976; Arstila 1997; Katz et al. 1966). This is especially important in associated vapours, where the concentration of monomers is exceeded by the concentration of some other cluster size with a negative formation energy. Acetic acid is an example of associated one-component systems (Heist et al. 1976) (in acetic acid dimers dominate), and sulphuric acid-water is an associated two-component system, where sulphuric acid forms hydrates (Jaecker-Voirol et al. 1987; Heist and Reiss 1974; Shugard et al. 1974; McGraw and Weber 1998; Hanson and Eisele 2000; Re et al. 1999), small clusters with one sulphuric acid and 1-3 water molecules which are more stable and thus more common than monomers.

We study $\overline{I}$ around the critical size and find the direction of $\overline{I}$ for the critical size. We express $\Delta\varphi$ as a two-variable Taylor series in the region around the critical size

$$\Delta\varphi = \Delta\varphi^* + \left(\frac{\partial \Delta\varphi}{\partial i}\right)_* (i-i^*) + \left(\frac{\partial \Delta\varphi}{\partial j}\right)_* (j-j^*) + \frac{1}{2}\left(\frac{\partial^2 \Delta\varphi}{\partial i^2}\right)_* (i-i^*)^2$$
$$+ \left(\frac{\partial^2 \Delta\varphi}{\partial i \partial j}\right)_* (i-i^*)(j-j^*) + \frac{1}{2}\left(\frac{\partial^2 \Delta\varphi}{\partial j^2}\right)_* (j-j^*)^2 + ...$$

The first derivatives are zero for the critical size,

$$\left(\frac{\partial \Delta\varphi}{\partial i}\right)_* = \left(\frac{\partial \Delta\varphi}{\partial j}\right)_* = 0.$$

We form a matrix $\underline{W}^*$ of the second derivatives of the free energy

$$\underline{W}^* = \begin{pmatrix} \left(\frac{\partial^2 \Delta\varphi}{\partial i^2}\right)_* & \left(\frac{\partial^2 \Delta\varphi}{\partial i \partial j}\right)_* \\ \left(\frac{\partial^2 \Delta\varphi}{\partial i \partial j}\right)_* & \left(\frac{\partial^2 \Delta\varphi}{\partial j^2}\right)_* \end{pmatrix}$$

and a vector $\Delta\overline{n}$ representing the size variables

$$\overline{\Delta n} = \begin{pmatrix} i - i^* \\ j - j^* \end{pmatrix}.$$

NOTE: i and j stand for the total numbers of molecules in the cluster, $N_{i,d}$*, not the bulk values,* $N_{i,l}$*.*

With the aid of these definitions the free energy around the critical size becomes

$$\Delta\varphi \approx \Delta\varphi^* + \frac{1}{2}\overline{\Delta n}^T \underline{W}^* \overline{\Delta n}.$$

We also approximate $\underline{R} \approx \underline{R}^*$ as in the one-component case and get

$$\overline{I} = -\underline{R}^* F^e \exp\left(\frac{-\Delta\varphi^*}{kT_0}\right) \exp\left(-\frac{1}{2kT_0}\overline{\Delta n}^T \underline{W}^* \overline{\Delta n}\right)$$
$$\cdot \nabla \left(\frac{C}{F^e \exp\left(\frac{-\Delta\varphi^*}{kT_0}\right) \exp\left(-\frac{1}{2kT_0}\overline{\Delta n}^T \underline{W}^* \overline{\Delta n}\right).} \right).$$

F^e and $\exp\left(\frac{\Delta\varphi^*}{kT_0}\right)$ are constants and can be taken out of the derivatives, and they cancel out to give

$$\overline{I} = -\underline{R}^* \exp\left(-\frac{1}{2kT_0}\overline{\Delta n}^T \underline{W}^* \overline{\Delta n}\right) \nabla \left(\frac{C}{\exp\left(-\frac{1}{2kT_0}\overline{\Delta n}^T W^* \overline{\Delta n}\right)} \right). \tag{5.21}$$

Coordinate transformations

Next we seek to change the variables so that we get rid of $\underline{R}^*$, as $\underline{R}^*$ couples the components of $\nabla\left(C/\exp(..)\right)$ with each other, and we want to have a clear situation where $I_x \propto \frac{\partial}{\partial x}\left(C/\exp(..)\right)$ and $I_y \propto \frac{\partial}{\partial y}\left(C/\exp(..)\right)$ (Trinkaus 1983). In order to achieve this we need to find a matrix $\underline{R}^{*1/2}$ for which $\underline{R}^{*1/2} \cdot \underline{R}^{*1/2} = \underline{R}^*$ and convert $\overline{\Delta n}$, $\overline{I}$, C and ∇ to new variables $\overline{\Delta \eta}$, $\overline{\iota}$, ξ and ∇_η using the following rules:

$$\overline{\Delta n} = \underline{R}^{*1/2}\overline{\Delta\eta}$$
$$\overline{I} = \frac{1}{\det\left(\underline{R}^{*1/2}\right)}\underline{R}^{*1/2}\overline{\iota}$$
$$C = \frac{\xi}{\det\left(\underline{R}^{*1/2}\right)}$$

$$\nabla \equiv \nabla_{i,j} = \left(\frac{\partial}{\partial i}, \frac{\partial}{\partial j}\right) = \underline{R}^{*-1/2}\overline{\nabla_\eta}$$
$$\nabla_\eta = \left(\frac{\partial}{\partial \Delta\eta_1}, \frac{\partial}{\partial \Delta\eta_2}\right).$$

We should keep in mind that $\underline{R}^*$, $\underline{W}^*$ and $\underline{R}^{*1/2}$ are real, symmetric matrices. The conversion for differential operator ∇ follows from the general rule (which you can check)

$$\overline{v} = \underline{A}\overline{u} \rightarrow \nabla_v = \left(A^T\right)^{-1}\nabla_u \tag{5.22}$$

in the symmetric case where $\underline{A} = \underline{R}^{*1/2} = \left(\underline{R}^{*1/2}\right)^T$. In terms of the new variables eq. (5.21) becomes

$$\frac{1}{\det\left(\underline{R}^{*1/2}\right)}\underline{R}^{*1/2}\cdot\bar{\iota} = -\underline{R}^{*}\exp\left(\frac{-1}{2kT_0}\left(\underline{R}^{*1/2}\overline{\Delta\eta}\right)^T\cdot\underline{W}^{*}\cdot\left(\underline{R}^{*1/2}\overline{\Delta\eta}\right)\right)$$

$$\cdot\,\underline{R}^{*-1/2}\nabla_\eta\left(\frac{\xi}{\det\left(\underline{R}^{*1/2}\right)}\cdot\exp\left(\frac{1}{2kT_0}\left(\underline{R}^{*1/2}\overline{\Delta\eta}\right)^T\cdot\underline{W}^{*}\left(\underline{R}^{*1/2}\overline{\Delta\eta}\right)\right)\right).$$

First we note that det $\left(R^{*1/2}\right)$ is a constant and cancels. On the right-hand side, the exponential is a scalar and we can combine $\underline{R}^{*}\cdot\underline{R}^{*-1/2} = \underline{R}^{*1/2}$ and thus also $\underline{R}^{*1/2}$ cancels from both sides. Now we insert a unity matrix $\underline{\mathbf{1}} = \underline{R}^{-1/2}\underline{R}^{1/2}$ into the interior of the exponentials

$$\left(\underline{R}^{*1/2}\overline{\Delta\eta}\right)^T\cdot\underline{W}^{*}\cdot\left(\underline{R}^{*1/2}\overline{\Delta\eta}\right) = \left(\underline{R}^{*1/2}\overline{\Delta\eta}\right)^T\underline{R}^{*-1/2}\underline{R}^{*1/2}\underline{W}^{*}\left(\underline{R}^{*1/2}\overline{\Delta\eta}\right).$$

You can show that $\left(\underline{R}^{*1/2}\overline{\Delta\eta}\right)^T\underline{R}^{*-1/2} = \overline{\Delta\eta}^T$ and the interior of the exponential becomes

$$\overline{\Delta\eta}^T\underline{R}^{*1/2}\underline{W}^{*}\underline{R}^{*1/2}\overline{\Delta\eta}.$$

We denote

$$\underline{\varGamma} = \underline{R}^{*1/2}\underline{W}^{*}\underline{R}^{*1/2}.$$

For the future it is important to note that $\underline{\varGamma}$ is a symmetric matrix as well. The flow in the new coordinates is

$$\bar{\iota} = -\exp\left(-\frac{1}{2kT_0}\overline{\Delta\eta}^T\underline{\varGamma}\,\overline{\Delta\eta}\right)\nabla_\eta\left(\xi\exp\left(\frac{1}{2kT_0}\overline{\Delta\eta}^T\underline{\varGamma}\,\overline{\Delta\eta}\right)\right). \tag{5.23}$$

To calculate $\overline{\Delta\eta}^T\underline{\varGamma}\,\overline{\Delta\eta}$ we want to find a coordinate system where $\underline{\varGamma}$ becomes diagonal. The axes of the new coordinate system are parallel to the eigenvectors $\overline{e}_\lambda$ of $\underline{\varGamma}$ and the diagonal elements of $\underline{\varGamma}$ are the eigenvalues λ which satisfy the following equation

$$\underline{\varGamma}\,\overline{e}_\lambda = \lambda\overline{e}_\lambda,$$

which in terms of $\underline{W}^{*}$ and $\underline{R}^{*}$ reads

$$\underline{R}^{*1/2}\underline{W}^{*}\underline{R}^{*1/2}\overline{e}_\lambda = \lambda\overline{e}_\lambda.$$

Since $\underline{\varGamma}$ is symmetric, $\overline{e}_{\lambda_1}$ and $\overline{e}_{\lambda_2}$ are orthogonal, and so are the axes of the new coordinate system, and the transformation from $\overline{\Delta\eta}$ to $\overline{\Delta\eta}'$, where the latter is in the eigenvector coordinates, is a pure rotation represented by an orthogonal matrix $\underline{O}$, (orthogonal matrix satisfies $\underline{O}\cdot\underline{O}^T = \underline{\mathbf{1}}$ and $\det\underline{O} = 1$). We express $\bar{\iota}$, $\Delta\eta_1$, $\underline{\varGamma}$, $\Delta\eta_2$ and ∇_η in this eigenvector system:

$$\begin{aligned}\overline{\Delta\eta}' &= \underline{O}\,\overline{\Delta\eta}\\ \overline{\iota}' &= \underline{O}\,\overline{\iota}\\ \underline{\Gamma'} &= \underline{O}\cdot\underline{\Gamma}\cdot\underline{O}^T\\ \nabla_{\eta'} &= \underline{O}\nabla_\eta\end{aligned}$$

The last of these transformations follows from the general rule (5.22) in the case of an orthogonal matrix $\underline{O}^T = \underline{O}^{-1}$. The whole point of this coordinate transformation is that in the eigenvalue coordinate system $\underline{\Gamma'}$ is diagonal

$$\underline{\Gamma'} = \underline{O}\cdot\underline{\Gamma}\cdot\underline{O}^T = \begin{pmatrix}\lambda_1 & 0\\ 0 & \lambda_2\end{pmatrix}$$

and

$$\overline{\Delta\eta'}^T\,\underline{\Gamma'}\,\overline{\Delta\eta'} = \Delta\eta_1'^2\lambda_1 + \Delta\eta_2'^2\lambda_2,$$

which means that eq. (5.23) can be written as

$$\begin{aligned}\overline{\iota}' = &-\exp\left(-\frac{1}{2kT_0}\left(\Delta\eta_1'^2\lambda_1+\Delta\eta_2'^2\lambda_2\right)\right)\\ &\cdot\nabla_{\eta'}\left(\xi\exp\left(\frac{1}{2kT_0}\left(\Delta\eta_1'^2\lambda_1+\Delta\eta_2'^2\lambda_2\right)\right)\right)\end{aligned}$$

and the directions $\overline{\iota}_1'$ and $\overline{\iota}_2'$ can be completely separated:

$$\begin{aligned}\iota_1' = &-\exp\left(-\frac{1}{2kT_0}\left(\Delta\eta_1'^2\lambda_1+\Delta\eta_2'^2\lambda_2\right)\right)\\ &\cdot\frac{\partial}{\partial\Delta\eta_1'}\left(\xi\exp\left(\frac{1}{2kT_0}\left(\Delta\eta_1'^2\lambda_1+\Delta\eta_2'^2\lambda_2\right)\right)\right)\end{aligned}\tag{5.24}$$

$$\begin{aligned}\iota_2' = &-\exp\left(-\frac{1}{2kT_0}\left(\Delta\eta_1'^2\lambda_1+\Delta\eta_2'^2\lambda_2\right)\right)\\ &\cdot\frac{\partial}{\partial\Delta\eta_2'}\left(\xi\exp\left(\frac{1}{2kT_0}\left(\Delta\eta_1'^2\lambda_1+\Delta\eta_2'^2\lambda_2\right)\right)\right).\end{aligned}\tag{5.25}$$

Using the rule for calculating the determinant of a product of matrices, $\det(\underline{AB}) = \det(\underline{A})\det(\underline{B})$, we get

$$\begin{aligned}\det\underline{\Gamma'} &= \det(\underline{O\Gamma O^T}) = 1\cdot\det(\underline{\Gamma})\cdot 1 = \det\left(\underline{R}^{*1/2}\underline{W}^*\underline{R}^{*1/2}\right)\\ &= \det\underline{R}^{*1/2}\det\underline{W}^*\det\underline{R}^{*1/2} = (\det\underline{R}^*)^{1/2}\det\underline{W}^*(\det\underline{R}^*)^{1/2}\\ &= \det\underline{R}^*\det\underline{W}^*.\end{aligned}$$

The determinant of the growth matrix is always positive since condensation coefficients are positive

$$\det(\underline{R}^*) = \det \begin{pmatrix} \beta_1^* & 0 \\ 0 & \beta_2^* \end{pmatrix} = \beta_1^* \beta_2^* > 0.$$

Even if we take cluster-cluster processes into account and $\underline{R}^*$ has non-zero off-diagonals and its determinant is always positive. Since the critical size is a saddle point in the free energy surface, the determinant of the second derivative matrix $\underline{W}^*$ is negative

$$\det(\underline{W}^*) = \det \begin{pmatrix} \left(\dfrac{\partial^2 \Delta\varphi}{\partial i^2}\right)_* & \left(\dfrac{\partial^2 \Delta\varphi}{\partial i \partial j}\right)_* \\ \left(\dfrac{\partial^2 \Delta\varphi}{\partial i \partial j}\right)_* & \left(\dfrac{\partial^2 \Delta\varphi}{\partial j^2}\right)_* \end{pmatrix} < 0.$$

Thus $\det \underline{\Gamma} < 0$. But $\det \underline{\Gamma} = \lambda_1 \lambda_2$, which means that one of the λ_1 and λ_2 must be positive and the other negative. We choose λ_1 as the negative eigenvalue. Even in systems with more than two components exactly one of the eigenvalues of matrix $\underline{\Gamma}$ is negative, corresponding to the only direction where the critical size is a maximum.

Now we assume that we have found the desired coordinates $x = \Delta\eta'_1$ and $y\Delta\eta'_2$: we believe that around the critical size the flow direction is constant and $\Delta\eta'_1$-axis is in the flow direction, in other words the flow $\overline{\iota'} \upuparrows \overline{e}_{\lambda_1}$ is in the direction of eigenvector for eigenvalue λ_1. Thus we have to have $\iota'_2 = 0$, which according to eq. (5.25) requires that

$$\frac{\partial}{\partial \Delta\overline{\eta}'_2} \left(\xi \exp\left(\frac{1}{2kT_0} \left(\Delta\eta_1'^2 \lambda_1 + \Delta\eta_2'^2 \lambda_2 \right) \right) \right) = 0$$

around the critical size. Furthermore, for a steady state ι'_1 must be independent of $x = \Delta\eta'_1$, but can depend on $y = \Delta\eta'_2$. In eq. (5.24) constants $\exp(\frac{\Delta\eta_2'^2 \lambda_2}{2kT_0})$ can be cancelled to give

$$\iota'_1 = -\exp\left(-\frac{1}{2kT_0} \left(\Delta\eta_1'^2 \lambda_1 \right) \right) \frac{\partial}{\partial \Delta\eta'_1} \left(\xi \exp\left(\frac{1}{2kT_0} \left(\Delta\eta_1'^2 \lambda_1 \right) \right) \right).$$

This equation can be rearranged as

$$\frac{\iota'_1}{\exp\left(-\dfrac{1}{2kT_0} \lambda_1 \Delta\eta_1'^2 \right)} = -\frac{\partial}{\partial \Delta\eta'_1} \left(\xi \exp\left(\frac{1}{2kT_0} \lambda_1 \Delta\eta_1'^2 \right) \right)$$

which we integrate from $\Delta\eta'_1 = -\infty$ to $\Delta\eta'_1 = \infty$. The origin of the $\Delta\eta'_1$, $\Delta\eta'_2$ coordinate system is the critical size:

$$\overline{\Delta n} = (i - i^*, j - j^*) = \underline{OR}^{*1/2} \overline{\Delta\eta}$$

$$\overline{\Delta n} = (0,0) \Leftrightarrow \overline{\Delta\eta'} = 0 \Leftrightarrow i = i^* \quad \text{and} \quad j = j^*.$$

Since $\Delta\eta_1 = \Delta\eta_2 = 0$ at the critical size, and as in the one-component case an integral from 0 to ∞ would leave some area very near the critical size out, we should start from $\Delta\eta_1' = -\infty$. Now ι_1' is constant in the integral with respect to $\Delta\eta_1'$

$$\iota_1' \int_{-\infty}^{\infty} \exp\left(\frac{-|\lambda_1|}{2kT_0}\Delta\eta_1^2\right) d\Delta\eta_1' = -\int_{-\infty}^{\infty} \xi \exp\left(\frac{1}{2kT_0}\lambda_1 \Delta\eta_1'^2\right),$$

where we have denoted $\lambda_1 = -|\lambda_1|$ to underline the fact that eigenvalue λ_1 is negative. We multiply both the nominator and denominator of the right-hand side by $F^e \exp\left(\frac{1}{2kT_0}\lambda_2\Delta\eta_2'^2\right) \exp\left(\frac{\Delta\varphi^*}{kT_0}\right)$ to get

$$\begin{aligned}
&\iota_1' \int_{-\infty}^{\infty} \exp\left(\frac{-|\lambda_1|}{2kT_0}\Delta\eta_1^2\right) d\Delta\eta_1' \\
&= -\int_{\Delta\eta_1'=-\infty}^{\Delta\eta_1'=\infty} \frac{C \det(\underline{R}^{*1/2}) F^e \overbrace{\exp\left(\frac{1}{2kT_0}(\lambda_1\Delta\eta_1'^2 + \lambda_2\Delta\eta_2'^2)\right)\exp\left(\frac{\Delta\varphi^*}{kT_0}\right)}^{\exp(\Delta\varphi/(kT_0))}}{F^e \exp\left(\frac{1}{2kT_0}\lambda_2\Delta\eta_2'^2\right)\exp\left(\frac{\Delta\varphi^*}{kT_0}\right)},
\end{aligned}$$

which can be rearranged to read

$$\begin{aligned}
&\iota_1' \int_{-\infty}^{\infty} \exp\left(\frac{-|\lambda_1|}{2kT_0}\Delta\eta_1^2\right) d\Delta\eta_1' \\
&= -\int_{\Delta\eta_1'=-\infty}^{\Delta\eta_1'=\infty} \frac{C \det(\underline{R}^{*1/2}) F^e}{F^e \exp\left(\frac{-\Delta\varphi}{kT_0}\right)\exp\left(\frac{1}{2kT_0}\lambda_2\Delta\eta_2'^2\right)\exp\left(\frac{\Delta\varphi^*}{kT_0}\right)} \\
&= -\det(\underline{R}^{*1/2}) F^e \exp\left(\frac{-\lambda_2\Delta\eta_2'^2}{2kT_0}\right)\exp\left(\frac{-\Delta\varphi^*}{kT_0}\right) \int_{\Delta\eta_1'=-\infty}^{\Delta\eta_1'=\infty} \frac{C}{F^e \exp\left(\frac{-\Delta\varphi}{kT_0}\right)},
\end{aligned} \tag{5.26}$$

where in the last stage all constants independent of the integration variable $\Delta\eta_1'$ have been collected in the beginning of the right-hand side expression. Assume that for $\Delta\eta_1' \to \infty$

$$\frac{C}{F^e \exp\left(\frac{-\Delta\varphi}{kT_0}\right)} \to 0$$

and for $\Delta\eta_1' \to -\infty$ (which is loosely like $(i,j) \to (0,1)$ or $(i,j) \to (1,0)$, see p. 93)

$$\frac{C}{F^e \exp\left(\dfrac{-\Delta\varphi}{kT_0}\right)} \to 1.$$

The left-hand side of eq. (5.26) is calculated with the help of the table integral

$$\int_{-\infty}^{\infty} \exp\left(-ax^2\right) dx = \sqrt{\frac{\pi}{a}}$$

and we get

$$\iota_1' \cdot \sqrt{\frac{2\pi kT_0}{|\lambda_1|}} = (-0+1) \cdot \det(\underline{R}^{*1/2}) F^e \exp\left(\frac{-\lambda_2 \Delta\eta_2^{'2}}{2kT_0}\right) \exp\left(\frac{-\Delta\varphi^*}{kT_0}\right)$$
$$= \det(\underline{R}^{*1/2}) F^e \exp\left(\frac{-\Delta\varphi^*}{kT_0}\right) \exp\left(-\frac{\lambda_2}{2kT_0}\Delta\eta_2^2\right),$$

which gives the flow as

$$\iota_1' = \sqrt{\frac{|\lambda_1|}{2\pi kT_0}} \det(\underline{R}^*)^{1/2} F^e \exp\left(\frac{-\Delta\varphi^*}{kT_0}\right) \exp\left(-\frac{\lambda_2}{2kT_0}\Delta\eta_2^2\right).$$

This result clearly reflects the assumption that ι_1' depends only on $\Delta\eta_2$ and not on $\Delta\eta_1$.

We still have to sum up ι_1' for all $\Delta\eta_2'$ to get the nucleation rate . The required integral over $\Delta\eta_2'$ is $\int_{-\infty}^{\infty} \exp\left(-\frac{\lambda_2}{2kT_0}\Delta\eta_2^{'2}\right) d\Delta\eta_2' = \sqrt{\frac{2\pi kT_0}{\lambda_2}}$ (remember that $\lambda_2 > 0$) and we get

$$\begin{aligned}
J &= \int_{-\infty}^{\infty} \iota_1' d\Delta\eta_2' \\
&= \sqrt{\frac{|\lambda_1|}{2\pi kT_0}} \det(\underline{R}^{*1/2}) F^e \exp\left(\frac{-\Delta\varphi^*}{kT_0}\right) \sqrt{\frac{2\pi kT_0}{\lambda_2}} \\
&= \frac{\sqrt{\dfrac{|\lambda_1|}{2\pi kT_0}} \det(\underline{R}^{*1/2}) F^e \exp\left(\dfrac{-\Delta\varphi^*}{kT_0}\right) \sqrt{\dfrac{|\lambda_1|}{2\pi kT_0}}}{\sqrt{\dfrac{|\lambda_1|}{2\pi kT_0}} \sqrt{\dfrac{\lambda_2}{2\pi kT_0}}} \\
&= \frac{|\lambda_1|}{2\pi kT_0} \frac{\det(\underline{R}^{*1/2}) F^e \exp\left(\dfrac{-\Delta\varphi^*}{kT_0}\right)}{\sqrt{\dfrac{|\lambda_1|\lambda_2}{2\pi kT_0 \cdot 2\pi kT_0}}},
\end{aligned}$$

where we have multiplied both the nominator and denominator with $\sqrt{\frac{\lambda_1}{2\pi kT_0}}$ since we seek to combine the terms to form the determinant

$$|\det(\underline{\Gamma})| = |\lambda_1|\lambda_2 = |\det(\underline{R}^*\underline{W}^*)| = |\det(\underline{R}^*)||\det(\underline{W}^*)|.$$

We move terms $\frac{1}{2\pi kT_0}$ which are under the square root inside the determinant using

$$\begin{aligned}\det(\frac{\underline{W}^*}{2\pi kT_0}) &= \det\begin{pmatrix} \frac{1}{2\pi kT_0}\left(\frac{\partial^2\Delta\varphi}{\partial i^2}\right)_* & \frac{1}{2\pi kT_0}\left(\frac{\partial^2\Delta\varphi}{\partial i\partial j}\right)_* \\ \frac{1}{2\pi kT_0}\left(\frac{\partial^2\Delta\varphi}{\partial i\partial j}\right)_* & \frac{1}{2\pi kT_0}\left(\frac{\partial^2\Delta\varphi}{\partial j^2}\right)_* \end{pmatrix} \\ &= \det(\underline{W}^*)\left(\frac{1}{2\pi kT_0}\right)^2\end{aligned}$$

and get the final form for the nucleation rate

$$J = \frac{|\lambda_1|}{2\pi kT_0}F^e \exp\left(\frac{-\Delta\varphi^*}{kT_0}\right)\cdot\frac{\sqrt{\det\underline{R}^*}}{\sqrt{\left|\det\left(\frac{\underline{W}^*}{2\pi kT_0}\right)\right|\det\underline{R}^*}}$$

$$\boxed{J = \frac{|\lambda_1|}{2\pi kT_0}F^e \exp\left(\frac{-\Delta\varphi^*}{kT_0}\right)\frac{1}{\sqrt{\left|\det\left(\frac{\underline{W}^*}{2\pi kT_0}\right)\right|}}. \qquad (5.27)}$$

This is a general result for multicomponent systems: λ_1 is always the only negative eigenvalue of product matrix $\underline{R}^*\underline{W}^*$. For two-component systems you see that $2\pi kT_0$ would actually cancel, but we have on purpose written the result in the form above since it works for any number of components. It should be noted that eq. (5.27) does not reduce to one-component nucleation rate in the case we set gas phase activities of all but one component to zero. The matrices involved in multicomponent nucleation theory have zero determinant if we set the number of molecules of some component to zero, and thus they do not have well-defined eigenvalues either. The same applies to reducing the n component formula to $n-1$ component formula in general.

In the original coordinates (i,j) the flow vector is given by

$$\overline{I} = \frac{1}{\det\left(\underline{R}^{*1/2}\right)}\left(\underline{R}^*\right)^{1/2}\overline{\imath} = \frac{1}{\det\left(\underline{R}^{*1/2}\right)}\left(\underline{R}^*\right)^{1/2}\cdot\underline{O}^T\overline{\imath'}$$

and we see that the transformation between $\overline{I}$ and $\overline{\iota}'$ is not a pure rotation, it changes the length scales as well $|\overline{I}| \neq |\iota|$, ($\underline{R}^{*1/2}$ is not orthogonal $\underline{R}^{*1/2}(\underline{R}^{*1/2})^T = \underline{R}^* \neq \mathbf{1}$). The direction of the critical size flow $\overline{\iota}$ in $(\Delta\eta_1,\Delta\eta_2)$ coordinates is given by the eigenvector of $\underline{R}^{*1/2}\underline{W}^*\underline{R}^{*1/2}$ related to the negative eigenvalue λ_1 satisfying

$$\underline{R}^{*1/2}\underline{W}^*\underline{R}^{*1/2}\overline{\iota} = \lambda_1\overline{\iota}$$

where

$$\overline{\iota} = \det(\underline{R}^{*1/2})\underline{R}^{*-1/2}\overline{I}.$$

In terms of the flow vector in original coordinates the eigenvalue equation reads

$$\underline{R}^{*1/2}\underline{W}^*\underline{R}^{*1/2}\det(\underline{R}^{*1/2})\underline{R}^{*-1/2}\overline{I} = \lambda_1\det(\underline{R}^{*1/2})\underline{R}^{*-1/2}\overline{I}$$

which simplifies to

$$\underline{R}^{*1/2}\underline{W}^* = \lambda_1\underline{R}^{*-1/2}\overline{I}$$

and by multiplying both sides with $\underline{R}^{*1/2}$ we get

$$\boxed{\underline{R}^*\underline{W}^*\overline{I} = \lambda_1\overline{I},} \tag{5.28}$$

which shows that λ_1 is also an eigenvalue of $\underline{R}^*\underline{W}^*$ and even in (i,j) coordinates the direction of $\overline{I}$ is that of the eigenvector of $\underline{R}^*\underline{W}^*$ related to the negative eigenvalue λ_1.

What has been said in chapter 5.2 about the $1/S$ factor applies also to multicomponent systems. The value used for the pre-factor F^e depends on whether supersaturated or true equilibrium has been used to calculate the evaporation coefficients. Self-consistency corrections to the equilibrium cluster distribution affect the value of F^e. In multicomponent systems F^e is often taken to be a sum of the monomer concentrations in either a nucleating or equilibrium vapour (see p. 83).

5.4 Usual formula for binary rate

Motivated by the one-component result (5.13) the two-component nucleation rate is often written in the form

$$\boxed{J = R_{av}F^e\exp\left(\frac{-\Delta\varphi^*}{kT_0}\right)Z,} \tag{5.29}$$

where R_{av} is called the average growth rate and Z is the Zeldovich factor. The Zeldovich factor is defined as

$$Z = \frac{-W^*_{x,y}(1,1)}{\sqrt{|\mathrm{det}\underline{W}^*|}}$$

and the average growth rate as

$$R_{av} = \frac{\det \underline{R}^*}{\beta_1^* \sin^2\theta + \beta_2^* \cos^2\theta - 2\beta_{1,2}^* \sin\theta\cos\theta},$$

where θ is the angle of the critical size flow in the (i,j)-coordinate system, and $\underline{W}^*_{x,y}$ is the second derivative matrix $\underline{W}^*$ in a coordinate system with the x-axis parallel to the critical size flow and the y-axis perpendicular to that. β_1^* and β_2^* are the diagonal and $\beta_{1,2}^*$ is the off-diagonal element of the growth matrix (the growth matrix is symmetric, which means that the off-diagonal elements, which are non-zero in associated vapours, are equal to each other). $\underline{W}^*_{x,y}$ can be calculated using the flow direction angle θ as

$$\begin{aligned}\underline{W}^*_{x,y} &= \begin{pmatrix} \cos\theta & \sin\theta \\ -\sin\theta & \cos\theta \end{pmatrix} \begin{pmatrix} W_{11} & W_{12} \\ W_{21} & W_{22} \end{pmatrix} \begin{pmatrix} \cos\theta & -\sin\theta \\ \sin\theta & \cos\theta \end{pmatrix} \\ &= \frac{W_{11} + 2W_{12}\tan\theta + W_{22}\tan^2\theta}{1+\tan^2\theta}\end{aligned}$$

where we have used notations
$W_{11} \equiv \left(\frac{\partial^2 \Delta\varphi}{\partial i^2}\right)_*$, $W_{12} \equiv \left(\frac{\partial^2 \Delta\varphi}{\partial i \partial j}\right)_*$ and $W_{22} \equiv \left(\frac{\partial^2 \Delta\varphi}{\partial j^2}\right)_*$
for the second derivatives of the free energy.

The flow angle θ can be calculated as before from the eigenvector of $\underline{R^*W^*}$, and in the two-component system $\tan\theta$ can be expressed with a compact analytical formula

$$\begin{aligned}\tan\theta =& \frac{-W_{11}\beta_1^* + W_{22}\beta_2^*}{2\left(W_{12}\beta_1^* + W_{22}\beta_{1,2}^*\right)} \\ &- \frac{\sqrt{4\left(W_{12}\beta_1^* + W_{22}\beta_{12}^*\right)\left(W_{11}\beta_{12}^* + W_{12}\beta_2^*\right) + \left(W_{11}\beta_1^* - W_{22}\beta_2^*\right)^2}}{2\left(W_{12}\beta_1^* + W_{22}\beta_{1,2}^*\right)}.\end{aligned} \tag{5.30}$$

Eq. (5.29) is the most widely used formula originally derived for two-component systems as the first multicomponent case in the 1970's (McDonald 1962; Stauffer 1976). Eq. (5.27) for two-component systems is actually identical to formula (5.29), which can rather easily be shown by finding the explicit formula of the eigenvalue λ_1 and comparing it with $W^*_{x,y}(1,1) \cdot R^*_{av}$, with θ given by eq. (5.30).

Often the nucleation rate (5.29) is simplified by setting the Zeldovich factor equal to one,

$$Z \approx 1$$

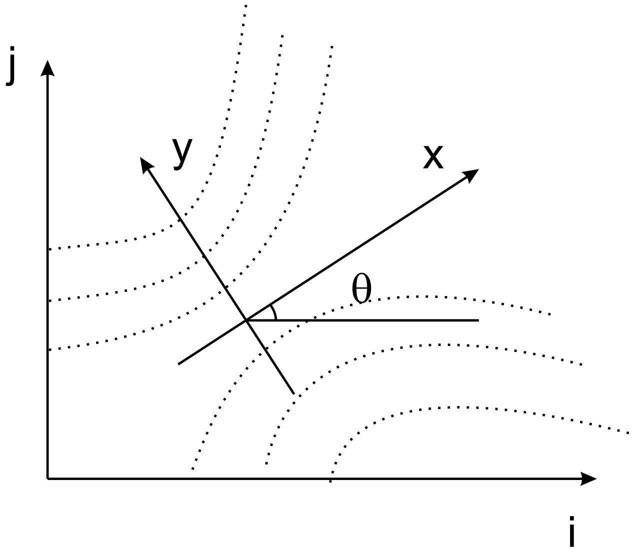


Fig. 5.6. The direction angle θ for the critical cluster flow (also called the saddle point flow) in a two-component system.

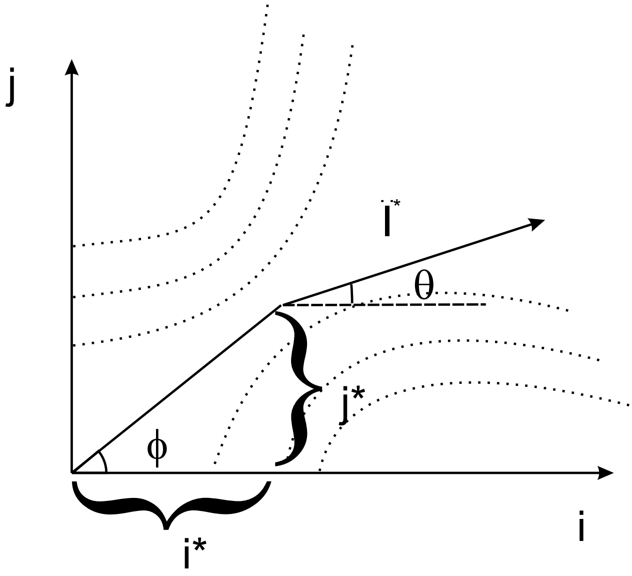


Fig. 5.7. The direction of the vector connecting the origin and the critical size ϕ is often used as an approximation for the flow direction θ.

or using the virtual monomer approach (Kulmala and Viisanen 1991) where the one-component Zeldovich factor (5.15)

$$Z = \sqrt{\frac{\sigma}{kT_0}} \frac{v_x^*}{2\pi r^{*2}} \tag{5.31}$$

is used for two-component systems with the virtual monomer volume defined as

$$v_x^* = (1 - x^*)v_{1,l}^* + x^* v_{2,l}^*, \tag{5.32}$$

where x^* is the mole fraction of component 2 in the critical cluster. In the simplified approaches the direction angle θ is calculated either simply from the direction angle ϕ of the vector connecting origin and critical size as shown in Fig. 5.7

$$\theta \approx \phi = \arctan\left(\frac{j^*}{i^*}\right). \tag{5.33}$$

or the *steepest descent* approximation. The steepest descent direction is the direction where the maximum of $\Delta\varphi$ is sharpest, and it can be found as the direction of the eigenvalue of matrix $\underline{W}^*$ connected to the negative eigenvalue of this second derivative matrix. The real direction of flow $\overline{I}^*$ deviates from the steepest descent because of the different condensation rates for components 1 and 2. If the concentration of vapour 1, for example, is much higher than that of vapour 2, the fact that molecules of substance 1 collide with the critical cluster much more often than molecules of type 2 bend the flow from the energetically optimal direction toward the axis representing component 1.

5.5 Comparison of classical theory predictions with experimental results

The classical theory often fails in predicting the temperature dependence of the experimental nucleation rates. With many substances, the theoretical nucleation rates are too low at low temperatures, and too high at high temperatures (Hung et al. 1989; Schmitt et al. 1982; Viisanen et al. 1993; Strey et al. 1986; Kacker and Heist 1985).

Fig. 5.8 shows experimental data (Wölk and Strey 2001) and classical predictions for water nucleation rates at different temperatures as function of saturation ratio. The S dependence of the classical nucleation rate is correct, but temperature dependence is different from the experiments, as at 259K the theoretical and experimental curves agree, but when the temperature gets lower the deviation starts to increase. Looking from the point of view of nucleation theorems (Chapter 6), a correct S dependence, but wrong temperature dependence suggests that the classical theory predicts the size of the critical cluster correctly, but fails in describing the energy of the cluster.

Fig. 5.9 shows similar behaviour for 1-pentanol; the theoretical nucleation rates are about four orders of magnitude too low compared to experiments, but

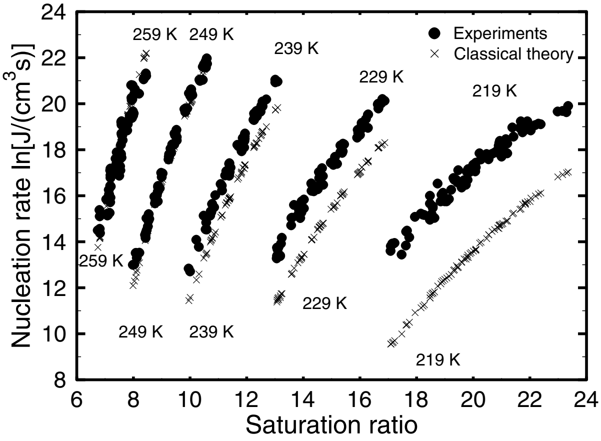


Fig. 5.8. Comparison of experimental nucleation rates (Wölk and Strey 2001) and classical theory predictions for water.

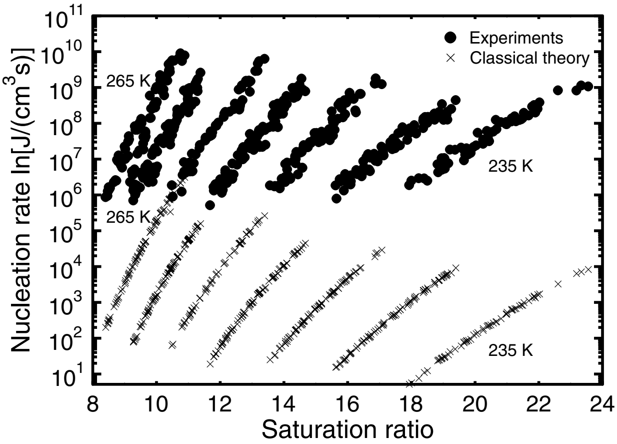


Fig. 5.9. Comparison of experimental nucleation rates (Iland et al. 2004) and classical theory predictions for 1-pentanol. The curves from left to right correspond to temperatures 265 K, 260 K, 255 K, 250 K, 245 K, 240 K and 235 K.

the saturation dependence is well predicted, and the temperature dependence is again erroneous.

Compared to experiments, classical theory also predicts too low critical supersaturations (too high nucleation rates) in associated vapours and highly polar fluids: heptonoic, decanoic and myristic acids (Agarwal and Heist 1980), acetic acid (Heist et al. 1976), formic and propanoic acid (Russell and Heist

1978), acetonitrile (Wright et al. 1991), benzonitrile, nitromethane and nitrobenzene (Wright et al. 1993).

Fig. 5.10 shows experimental sulphuric acid-water nucleation rates (Viisanen et al. 1997) at 298K and at two different relative humidities as a function of sulphuric acid vapour phase concentration. The diagonal lines represent the uncertainty regions of the experimental results. Also the classical predictions are shown.

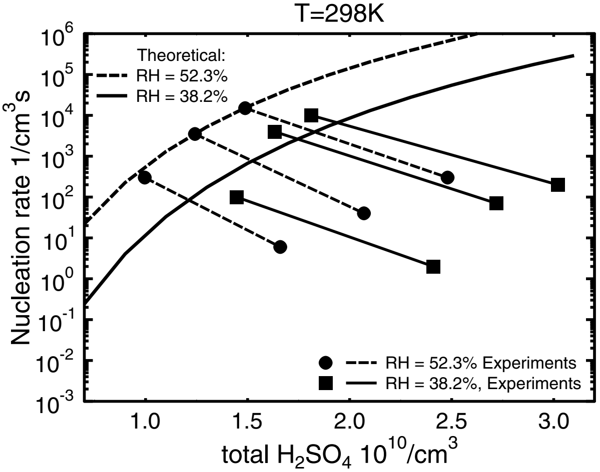


Fig. 5.10. Comparison of experimental results (Viisanen et al. 1997) and classical theory predictions for water-sulphuric acid nucleation rate as a function of sulphuric acid concentration in vapour phase. The acid concentration includes all the molecules in the vapour phase, also those bound to small stable pre-critical clusters (hydrates).

Considering the number of approximations used on the way the theory does quite well, especially in predicting the sulphuric acid dependence of the nucleation rate. This is however only true for systems with no or weak surface activity. In two-component systems, where strong surface enrichment occurs (e.g. water-alcohol systems), classical theory can predict unphysical behaviour, a decrease in the nucleation rate with increasing vapour pressures (Schmitt et al. 1990; Oxtoby and Kashchiev 1994; Strey et al. 1992), as shown for water-ethanol on p. 124.

Problems

5.1. Derive an explicit formula for one-component evaporation coefficients starting from eq. (5.6). Show that with approximation $A(n+1) - A(n) = \frac{dA}{dn}$

the equilibrium coefficient reduces to

$$\gamma_{clu} = \left(\frac{8\pi kT(m_{clu}+m_1)}{m_1 m_{clu}}\right)^{1/2} (r_{clu}+r_1)^2 \frac{P_e^o(T)}{kT} \exp\left(\frac{2m_1\sigma}{\rho_l kT r_{clu}}\right).$$

Show that the same result follows from calculating the evaporation coefficient from the equality of condensation rate and evaporation rate for a single spherical droplet which is in equilibrium with the surrounding vapour.

5.2. Plot the evaporation coefficient (independent of saturation ratio!) and condensation coefficient of water for saturation ratios $S = 4$, 6, and 8 at temperature 290K an a function of cluster radius. Identify critical cluster sizes from the equality of evaporation and condensation rates, and compare with critical sizes obtained from the Kelvin equation.

The saturation vapour pressure of water is (T in Kelvin)
$P_e = \exp[77.34 - 7235.42/T - 8.2\ln(T) + 0.00571T]$ Pa.
Density of liquid water is
$\rho_l = (1049.572 - 0.1763T)$ kg/m^3.
Molar mass of water is 18.02 g/mol.
Surface tension of pure water is
$\sigma = (0.117 - 0.152 \cdot 10^{-3}T)$ N/m.
Water vapour is assumed to be an ideal gas, and liquid is assumed incompressible.

5.3. Plot the pure water nucleation rate as a function of
a) relative humidity at $T=$ 263K and $T=$ 298K
b) as a function of temperature with constant RH=500%
c) as a function of temperature with constant vapour concentration $\rho_g=$ 6.33 mol/m^3.

The saturation vapour pressure of water is (T in Kelvin)
$P_e = \exp[77.34 - 7235.42/T - 8.2\ln(T) + 0.00571T]$ Pa.
Density of liquid water is
$\rho_l = (1049.572 - 0.1763T)$ kg/m^3.
Molar mass of water is 18.02 g/mol.
Surface tension of pure water is
$\sigma = (0.117 - 0.152 \cdot 10^{-3}T)$ N/m.

5.4. For pure ethanol at T=298K plot the nucleation rate as a function of saturation ratio using
a) eq. (5.13) resulting from integration
b) accurate eq. (5.10) with the sum
(test how large of an upper limit of the sum ($\mathcal{N}$) you have to choose so that the result does not change significantly if you increase $\mathcal{N}$ further)
c) same as a) but assuming the Zeldovich factor Z=1.

The saturation vapour pressure of ethanol is (T in Kelvin)
$P_{e,e} = \exp(69.3268 - 7055.3056/T - 6.41 \ln(T))$ Pa.
Density of liquid ethanol is
$\rho_l = 1037.31 - T \cdot 0.845941 \mathrm{kg/m^3}$ and
surface tension is
$\sigma = 0.04794 - T \cdot 0.08807 \cdot 10^{-3}$ N/m.
Molar mass of ethanol is 46.07 g/mol.

5.5. Show that for any geometry where the surface area is $A \propto n^{2/3}$, the one-component Zeldovich factor

$$Z = \sqrt{\frac{-1}{2\pi kT}\left(\frac{\partial^2 \Delta\varphi}{\partial n^2}\right)^*}$$

can be written as

$$Z = \sqrt{\frac{\Delta\varphi^*}{3\pi kT n^{*2}}}.$$

5.6. a) Calculate explicitly $\overline{\Delta n}^T \underline{W}^* \overline{\Delta n}$
b) Show that $\nabla = ((\underline{A})^T)^{-1} \nabla_{\Delta\eta}$, where
$\nabla = (\frac{\partial}{\partial i}, \frac{\partial}{\partial j})$
$\nabla_\eta = \left(\frac{\partial}{\partial \Delta\eta_1}, \frac{\partial}{\partial \Delta\eta_2}\right)$
$\overline{\Delta n} = \begin{pmatrix} i - i^* \\ j - j^* \end{pmatrix}$
$\overline{\Delta n} = \underline{A}\overline{\Delta\eta}$.
What is the result if $\underline{A}$ is a real, symmetric matrix?
What if $\underline{A}$ is an orthogonal matrix ($\underline{A}^T = \underline{A}^{-1}$)?
c) Calculate $\left(\underline{R}^{*1/2}\overline{\Delta\eta}\right)^T \underline{R}^{*-1/2}$
when $\underline{R}^{-1/2}\underline{R}^{1/2} = \underline{\mathbf{1}}$ and both $\underline{R}^{-1/2}$ and $\underline{R}^{1/2}$ are real, symmetric matrices.

5.7. Calculate the nucleation rate for mixture of n-octane and i-octane at the following experimental points and compare with experimental results.

T/K	$\mathcal{A}_{n,g}$	$\mathcal{A}_{i,g}$	$J_{\mathrm{exp}}/(\mathrm{cm^3 s})$
226	25.32	12.48	300.18
226	12.70	18.76	246.70
226	38.28	6.29	3215.40

Use the binary nucleation rate in the form

$$J = R_{av} Z F^e \exp(-\Delta G^*/(kT)).$$

You can take F^e as the sum of monomer concentrations in pure saturated vapours and

a) use approximation $Z \approx 1$
b) use the one-component Zeldovich factor (5.31) based on the virtual monomer concept.

Densities of pure i- and n-octane ($\mathrm{kg/m^3}$) are
$\rho_{i,l} = 10^3\{0.93769777 - 0.71540871 \cdot 10^{-3}T - [10.661614/(591.47583 - T)]\}$
$\rho_{n,l} = 10^3\{0.94450295 - 0.69548492 \cdot 10^{-3}T - [12.603612/(624.03296 - T)]\}$
In an ideal liquid mixture, the density is
$\rho_l(x_{\mathrm{mass}}, T) = \rho_{n,l}\rho_{i,l}/[(1 - x_{\mathrm{mass}})\rho_{i,l} + x_{\mathrm{mass}}\rho_{n,l}]$.
Surface tensions of pure i- and n-octane (N/m) are
$\sigma_i = (44.7778 - 0.0887439T)10^{-3}$ and
$\sigma_n = (49.4838 - 0.0951049T)10^{-3}$.
In an ideal liquid mixture, the surface tension is
$\sigma(x_{\mathrm{mol}}) = (1 - x_{\mathrm{mol}})\sigma_n + x_{\mathrm{mol}}\sigma_i$.
The saturation vapour pressures of pure compounds $P^o_{i,e}$ and $P^o_{n,e}$ (Pa) are given by:
$P^o_{i,e} = P_{i,c} \cdot \exp[(1/(1 - x_i)) \cdot (A_i x_i + B_i x_i^{1.5} + C_i x_i^3 + D_i x_i^6)]$ and
$P^o_{n,e} = P_{n,c} \cdot \exp[(1/(1 - x_n)) \cdot (A_n x_n + B_n x_n^{1.5} + C_n x_n^3 + D_n x_n^6)]$, where
$P_{i,c} = 2568 \cdot 10^3$, $T_{i,c} = 543.957$, $x_i = 1 - (T/T_{i,c})$,
$A_i = -7.6501166$, $B_i = 1.8899385$,
$C_i = -4.2070574$, $D_i = -0.22322060$,
$P_{n,c} = 2488 \cdot 10^3$, $T_{n,c} = 568.841$, $x_n = 1 - (T/T_{n,c})$,
$A_n = -8.1621949$, $B_n = 2.1052126$,
$C_n = -5.4163890$ and $D_n = -0.15830507$.
In an ideal liquid mixture, the activities are
$\mathcal{A}_{i,l} = x_{\mathrm{mol}}$
$\mathcal{A}_{n,l} = 1 - x_{\mathrm{mol}}$.
Molar masses are m_i=m_n=144.23g/mol.
In these formulae T is always in Kelvin,
x_{mol} is the mole fraction of i-octane and x_{mass} is the mass fraction of i-octane.
Experimental data and thermodynamic properties are taken from Doster et al. Journal of Chemical Physics Vol 113, pages 7197-7203 (note that they have a wrong formula for the density of an ideal mixture).

6

Nucleation theorems

Now we study how the formation free energy and the nucleation rate depend on gas phase activities and temperature. The results obtained in this chapter are very useful in gaining insight into the critical cluster properties by using experimental data for nucleation rate.

The applicability of nucleation theorems is not restricted to classical nucleation theory. The theorems are independent of the model we use for the cluster, and they can be derived based on general statistical mechanical considerations.

In this book we operate within classical theory, and derive the theorems based on classical formation free energy. The formation free energy of the critical cluster is given by (see p. 54):

$$\Delta\varphi^* = (P_0^* - P_l^*)\, V_l^* + A^*\sigma^*. \tag{6.1}$$

The underlying idea in the differentials of this chapter is that we change the vapour properties and temperature, but our cluster size and composition change accordingly so that the cluster is a critical cluster all the time. The total differential of the critical cluster formation free energy is

$$d\,(\Delta\varphi^*) = (dP_0 - dP_l^*)\, V_l^* + (P_0 - P_l^*)\, dV_l^* + A^* d\sigma^* + \sigma^* dA^*.$$

Equilibrium conditions are always valid for the critical cluster and thus

$$(P_l^* - P_0) = \sigma \frac{dA^*}{dV^*} = \frac{2\sigma^*}{r^*},$$

with the help of which we see that the second and third terms of $d\,(\Delta\varphi^*)$ cancel in the following way:

$$\left(P_0 - P_l^*\right) dV_l^* + \sigma^* dA^* = \frac{2\sigma^*}{r^*} dV_l^* + \sigma^* dA^* = dV^* \left(\frac{-2\sigma^*}{r^*} + \sigma^* \frac{dA^*}{dV^*} \right) = 0,$$

and we are left with the differential

$$d\left(\Delta\varphi^*\right) = \left(dP_0 - dP_l^*\right) V_l^* + A^* d\sigma^*. \tag{6.2}$$

The Gibbs-Duhem equation (1.9) for the vapour phase gives

$$V_g^* dP_0 - \mathcal{S}_g^* dT_0 = \sum N_{i,g}^* d\mu_{i,g}^0 \Rightarrow V_g^* dP_0 = \sum N_{i,g}^* d\mu_{i,g}^0 + \mathcal{S}_g^* dT_0$$

and for the liquid phase

$$V_l^* dP_l^* - \mathcal{S}_l^* dT_0 = \sum N_{i,l}^* d\mu_{i,l}^* \Rightarrow V_l^* dP_l^* = \sum N_{i,l}^* d\mu_{i,l}^* + \mathcal{S}_l^* dT_0.$$

The Gibbs adsorption equation for the surface phase gives

$$-\mathcal{S}_s^* dT_0 = \sum N_{i,s}^* d\mu_{i,s}^* + A^* d\sigma^* \Rightarrow A^* d\sigma^* = -\sum N_{i,s}^* d\mu_{i,s}^* - \mathcal{S}_s^* dT_0.$$

P_0, T_0 and $\mu_{i,g}^0$ are the intensive properties of the gas that we change; $N_{i,g}^*$, $N_{i,l}^*$, $N_{i,s}^*$, V_l^*, V_g^*, V_s^*, $\mu_{i,l}^*$, $\mu_{i,v}^*$, A^* and σ^* follow so that the cluster stays critical. Eq. (6.2) can now be written in the form

$$\begin{aligned} d\left(\Delta\varphi^*\right) =& \frac{V_l^*}{V_g^*} V_g^* dP_0 - V_l^* dP_l^* + A^* d\sigma^* \\ =& \frac{V_l^*}{V_g^*} \left(\sum N_{i,g}^* d\mu_{i,g}^0 + \mathcal{S}_g^* dT_0 \right) - \sum N_{i,l}^* d\mu_{i,l}^* + \mathcal{S}_l^* dT_0 \\ & - \sum N_{i,s}^* d\mu_{i,s}^* + \mathcal{S}_s^* dT_0. \end{aligned}$$

Since the cluster is always in equilibrium, the chemical potentials are equal in different phases

$$\mu_{i,s}^* = \mu_{i,l}^* = \mu_{i,g}^0$$

and the differential of the formation free energy is

$$\begin{aligned} d\left(\Delta\varphi^*\right) &= -\sum_i \left(N_{i,l}^* + N_{i,s}^* - \frac{V_l^*}{V_g^*} N_{i,g}^* \right) d\mu_{i,g}^0 \\ &\quad - \left(\mathcal{S}_l^* + \mathcal{S}_s^* - \frac{V_l^*}{V_g^*} \mathcal{S}_g^* \right) dT_0 \\ &= -\sum_i \left(N_{i,d}^* - \frac{V_l^*}{V_g^*} N_{i,g}^* \right) d\mu_{i,g}^0 \\ &\quad - \left(\mathcal{S}_d^* - \frac{V_l^*}{V_g^*} \mathcal{S}_g^* \right) dT_0, \end{aligned} \tag{6.3}$$

where we have defined the total entropy of the cluster as a sum of bulk liquid and surface contributions $\mathcal{S}_d^* = \mathcal{S}_l^* + \mathcal{S}_s^*$ in the same way as we have done for the molecular numbers $N_{i,d}^* = N_{i,l}^* + N_{i,s}^*$. Various terms in eq. (6.3) can be understood as follows:

$\frac{N_{i,g}^*}{V_g^*}$ is the average density of molecules i in the vapour.

$V_l^* \frac{N_{i,g}^*}{V_g^*}$ tells how many molecules of type i would fit to the volume of the cluster if it was filled with vapour.

$\Delta N_i^* \equiv N_{i,d}^* - V_l^* \frac{N_{i,g}^*}{V_g^*}$ tells the difference in number of molecules if there is a cluster in volume V_l^* compared to the same volume being filled with vapour (see Fig. 6.1).

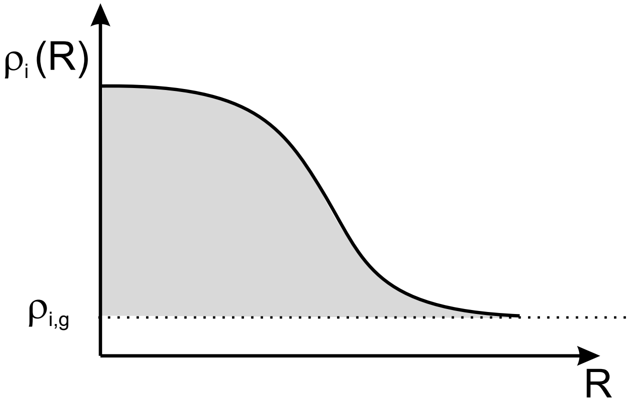


Fig. 6.1. The difference in number of molecules between volume $V_l^* = 4/3\pi r^3$ containing a cluster and the same volume containing only homogeneous vapour.

$\frac{\mathcal{S}_g^*}{V_g^*}$ is the entropy per unit volume in the vapour, and $\Delta\mathcal{S}^* = \mathcal{S}_d^* - \frac{V_l^*}{V_g^*}\mathcal{S}_g^*$ is the entropy increase due to cluster formation. With these definitions we get

$$d(\Delta\varphi^*) = -\sum_i \Delta N_i^* d\mu_{i,g}^0 - \Delta S^* dT_0.$$

If we take the derivative with respect to vapour phase chemical potential $\mu_{i,g}^0$ of one component i, keeping the other chemical potentials in the vapour $\mu_{j\neq i,g}^0$ constant we get the most general form of the first nucleation theorem [1]

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[1] NOTE: This relation is a close relative to the basic equation $N_i = -\left(\frac{\partial \Omega}{\partial \mu_i}\right)_{T,V,\mu}$

$$\boxed{\left(\frac{\partial \Delta\varphi^*}{\partial \mu_{i,g}^0}\right)_{T_0,\mu^0_{j\neq i,g}} = -\Delta N_i^*. \qquad (6.4)}$$

If the derivative is taken with respect to temperature keeping all gas phase chemical potentials $\mu^0_{i,g}$, and T_0 constant we get the most general form for the second nucleation theorem [2]

$$\boxed{\left(\frac{\partial \Delta\varphi^*}{\partial T_0}\right)_{\mu^0_{i,g}} = -\Delta\mathcal{S}^*. \qquad (6.5)}$$

6.1 First nucleation theorem

First we study the derivative of formation free energy with respect to chemical potential $\mu^0_{i,g}$ (Viisanen et al. 1993; Oxtoby and Kashchiev 1994; Kashchiev 1982). We want to know the partial derivative of $\frac{\Delta\varphi^*}{kT_0}$ with respect to $\ln\mathcal{A}_{i,g}$ since the former appears in the expression of the nucleation rate, and the nucleation rate is usually measured as a function of gas phase activities $\mathcal{A}_{i,g}$. We use the logarithm of the activity for convenience only.

The rules for changing variables in partial derivatives give

$$\left(\frac{\partial\frac{\Delta\varphi^*}{kT_0}}{\partial\ln\mathcal{A}_{i,g}}\right)_{\mu^0_{j,g},T_0} = \left(\frac{\partial\frac{\Delta\varphi^*}{kT_0}}{\partial\mu^0_{i,g}}\right)_{T_0,\mu^0_{j,g}}\left(\frac{\partial\mu^0_{i,g}}{\partial\ln\mathcal{A}_{i,g}}\right)_{T_0,\mu^0_{j,g}}. \qquad (6.6)$$

We calculate the derivative of chemical potential with respect to gas phase activity $(\partial\mu^0_{i,g}/\partial\ln\mathcal{A}_{i,g})_{T_0,\mu^0_{j,g}}$. If the vapour with pressure P_0 is a mixture of ideal gases with mole fractions $x_{i,g}$, each vapour behaves as if it was alone and having pressure $x_{i,g}P_0$. Using the Maxwell equation (2.13) and ideal gas law we get (see p. 30)

$$\begin{aligned}\mu^0_{i,g} =& \mu^p_{i,g}(x_{i,g}P_0) = \mu^p_{i,g}(P^p_{i,e}) + \int_{P^p_{i,e}}^{x_{i,g}P_0} d\mu_{i,g} \\ =& \mu^p_{i,g}(P^p_{i,e}) + \int_{P^p_{i,e}}^{x_{i,g}P_0}\frac{kT_0}{P}dP = \mu^p_{i,g}(P^p_{i,e}) + kT_0\ln\left(\frac{x_{i,g}P_0}{P^p_{i,e}}\right) \\ =& \mu^p_{i,g}(P^p_{i,e}) + kT_0\ln\mathcal{A}_{i,g}.\end{aligned}$$

---

[2] NOTE: This is closely linked with the basic relation $\mathcal{S} = -\left(\frac{\partial\Omega}{\partial T}\right)_{V,\mu}$

$P^p_{i,e}(T_0)$ is the saturation vapour pressure of pure component i and does not depend on the activity, but only on temperature, and also the chemical potential of pure i, $\mu^p_{i,g}(P^p_{i,e})$, depends only on temperature, and we get

$$\left(\frac{\partial \mu^0_{i,g}}{\partial \ln \mathcal{A}_{i,g}}\right)_{T_0,\mu^0_{j,g}} = kT_0. \tag{6.7}$$

We also see that when temperature is kept constant, keeping chemical potentials $\mu_{j,g}$ constant is equivalent to keeping gas phase activities $\mathcal{A}_{i,g}$ constant. Inserting result (6.7) together with the general form of the first nucleation theorem (6.4) to eq. (6.6) we get the ideal gas form for the free energy version of the first nucleation theorem ($1/(kT_0)$ is just a constant when taking the derivative)

$$\boxed{\left(\frac{\partial \frac{\Delta\varphi^*}{kT_0}}{\partial \ln \mathcal{A}_{i,g}}\right)_{\mathcal{A}_{j,g},T_0} = -\frac{1}{kT_0} kT_0 \Delta N^*_i = -\Delta N^*_i. \qquad (6.8)}$$

The nucleation rate is given by $J = C^* Z \exp\left(\frac{-\Delta\varphi^*}{kT_0}\right)$. If C^* and Z are weak functions of $\mathcal{A}_{i,g}$, we get the most readily applicable form of the first nucleation theorem

$$\boxed{\left(\frac{\partial \ln J}{\partial \ln \mathcal{A}_{i,g}}\right)_{\mathcal{A}_{j,g},T_0} \approx \Delta N^*_i. \qquad (6.9)}$$

For a one-component case it is easy to show that the contribution of the pre-exponential equals 1 and

$$\left(\frac{\partial \ln J}{\partial \ln S}\right)_{T_0} = \Delta N^* + 1.$$

Also for multicomponent cases the contribution of the pre-exponential is of the order of 1. The first nucleation theorem can be used in two directions (for simplicity in one-component systems):

1. If you know how the nucleation rate depends on the saturation ratio at constant temperature, you know the critical size as a a function of saturation ratio. Remember that the theorem is actually model independent, so the critical size you obtain is not dependent on the classical droplet model.
2. If you know experimentally the nucleation rate J_0 at one saturation ratio S_0 (and temperature T_0) together with the critical size as a function of saturation ratio S you can predict the S-dependence of the nucleation rate:
$$\ln\left(\frac{J}{J_0}\right) = \int_{S_0}^{S} \Delta N^* d(\ln S) = \int_{S_0}^{S} \frac{\Delta N^*}{S} dS.$$
The critical size can be obtained, for example, with computer simulations.

6.2 Activity plots

Often experimentalists have measured the onset conditions where a certain nucleation rate J_0 is observed. The gas phase activity needed to produce a certain threshold nucleation rate (if not explicitly mentioned, often $J_0 = 1/(\mathrm{cm}^3\mathrm{s})$) is called the *critical gas phase activity* (in a one-component system *critical saturation ratio* or the *critical supersaturation*).

In two-component systems these results can be expressed in the form of activity plots: The gas phase activity of component 2 as a function of the gas phase activity of component 1 for constant temperature and constant nucleation rate (see Fig. 6.2). To derive the slope of the activity plot in terms of critical cluster properties we use the general partial derivative identity:

$$\left(\frac{\partial A}{\partial B}\right)_C \left(\frac{\partial B}{\partial C}\right)_A \left(\frac{\partial C}{\partial A}\right)_B = -1$$

for $\ln J$, $\ln \mathcal{A}_{i,g}$ and $\ln \mathcal{A}_{j,g}$ and get

$$\left(\frac{\partial \ln J}{\partial \ln \mathcal{A}_{i,g}}\right)_{\mathcal{A}_{j,g},T_0} \left(\frac{\partial \ln \mathcal{A}_{i,g}}{\partial \ln \mathcal{A}_{j,g}}\right)_{\ln J,T_0} \left(\frac{\partial \ln \mathcal{A}_{j,g}}{\partial \ln J}\right)_{\mathcal{A}_{i,g},T_0} = -1.$$

Using the first nucleation theorem for the first and third partial derivatives this becomes

$$\Delta N_i^* \left(\frac{\partial \ln \mathcal{A}_{i,g}}{\partial \ln \mathcal{A}_{j,g}}\right)_{\ln J,T_0} \frac{1}{\Delta N_j^*} = -1,$$

which gives

$$\boxed{\left(\frac{\partial \ln \mathcal{A}_{i,g}}{\partial \ln \mathcal{A}_{j,g}}\right)_{\ln J,T_0} = -\frac{\Delta N_j^*}{\Delta N_i^*}.} \tag{6.10}$$

So if we plot $\mathcal{A}_{i,g}$ as a function of $\mathcal{A}_{j,g}$ for constant nucleation rate, the slope of the curve is $-\dfrac{\Delta N_j^*}{\Delta N_i^*}$.

Fig. 6.2 shows an activity plot for a water-ethanol mixture, constant nucleation rate $J = 10^7/(\mathrm{cm}^3\mathrm{s})$ (Viisanen et al. 1994). The "hump" seen in the theoretical prediction for water-ethanol is typical for surface active systems. For the uphill part $\left(\dfrac{\partial \ln \mathcal{A}_{i,g}}{\partial \ln \mathcal{A}_{j,g}}\right)_{\ln J,T_0} > 0$, which means according to eq. (6.10) that $\Delta N_j^* < 0$ or $\Delta N_i < 0$. This is clearly an unphysical result and it is caused by the assumption that the equimolar surface and the surface of tension coincide. When plotting the nucleation rate as a function of supersaturation, the same problem causes the nucleation rate to decrease with increasing supersaturation as seen in Fig. 6.3

$$\left(\frac{\partial \ln J}{\partial \ln \mathcal{A}_{i,g}}\right)_{\mathcal{A}_{j,g},T_0} \approx \Delta N_i^* < 0.$$

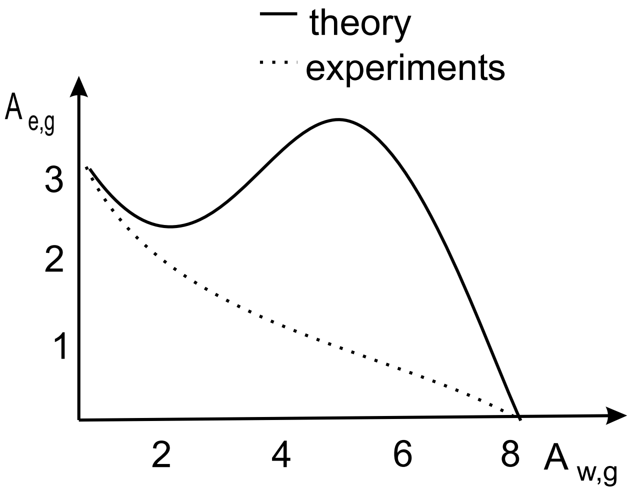

Fig. 6.2. Activity plot for water-ethanol nucleation at temperature 260K and nucleation rate $J_0 = 10^7/(\mathrm{cm}^3\mathrm{s})$. Experimental results from Viisanen et al. (1994).

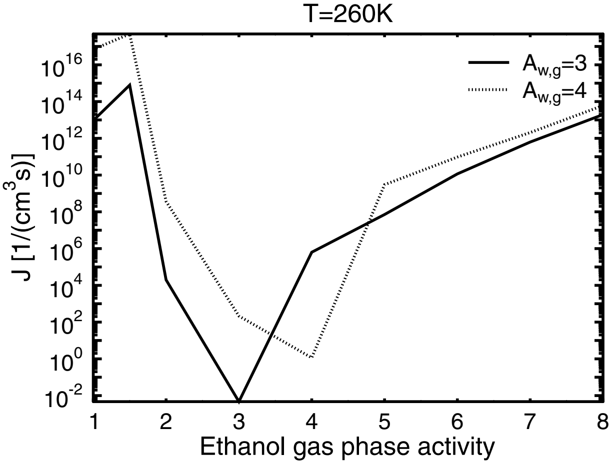

Fig. 6.3. Theoretical nucleation rate in water-ethanol system at temperature 260K for two gas phase activities of water. We have used eq. (5.29) with flow direction (5.33) and Zeldovich factor equal to one. (Due to the negative molecular number an accurate Zeldovich factor can not be rigorously evaluated.)

6.3 Clausius-Clapeyron equation and the order of phase transition

To derive a practical form for the second nucleation theorem we need the Clausius-Clapeyron equation. If we have vapour and liquid in equilibrium (flat surface and one-component case) the temperature, pressure and chemical potential are the same on both sides of the surface.

The Gibbs free energy of each of the phases can be written as

$$G = U + PV - T\mathcal{S} = T\mathcal{S} - PV + \mu N + PV - T\mathcal{S} = \mu N$$

where we have used the fundamental equation $U = T\mathcal{S} - PV + \mu N$. When N molecules change phase at equilibrium, their Gibbs free energy stays constant since chemical potentials in coexisting phases are equal $\mu_g = \mu_l$,

$$G_g = \mu_g N = \mu_l N = G_l.$$

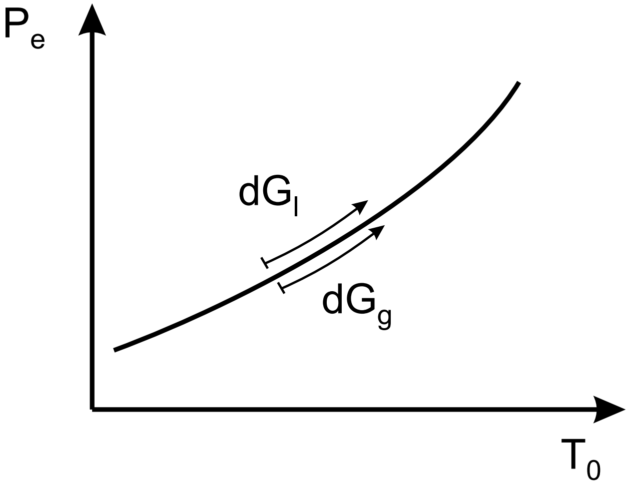

Fig. 6.4. The Gibbs free energy change along the phase equilibrium curve.

When we move along the *co-existence* curve (Fig. 6.4), the Gibbs free energy on the gas side changes as (see p. 46)

$$dG_g = -\mathcal{S}_g dT_g + V_g dP_g + \mu_g dN$$

and on the liquid side the change is

$$dG_l = -\mathcal{S}_l dT_l + V_l dP_l + \mu_l dN.$$

The number of molecules in our theoretical sample is kept constant, $dN = 0$, and equilibrium conditions guarantee that $dP_g = dP_l = dP_e^p$, $dT_g = dT_l = dT_0$, and the free energy changes can be simplified to

$$dG_g = -\mathcal{S}_g dT_0 + V_g dP_e^p$$

and

$$dG_l = -\mathcal{S}_l dT_0 + V_g dP_e^p .$$

Since $G_g = G_l$, the changes of free energies in gas and liquid must be equal, $dG_g = dG_l$, and we get

$$(\mathcal{S}_g - \mathcal{S}_l)\, dT_0 = (V_g - V_l)\, dP_e^p$$

$$\left(\frac{\partial P_e^p}{\partial T_0}\right)_{\mathrm{coex}} = \frac{\mathcal{S}_g - \mathcal{S}_l}{V_g - V_l}$$

Using the definition of enthalpy (p. 47), the temperature can be expressed as $T = \left(\frac{\partial H}{\partial \mathcal{S}}\right)_{P,N}$, which gives $\mathcal{S}_g - \mathcal{S}_l = \frac{\Delta H^{p,e}}{T_0}$ when P, N are constants and $\Delta H^{p,e} = H_g - H_l$ is the latent heat or phase transition enthalpy. We have emphasized the fact that we are dealing with a pure one-component system by the superscript ^{p} in the latent heat. Latent, in other words hidden, heat means heat flow in or out of the system without change of temperature. The counterpart of latent heat is sensible heat, meaning heat flow resulting in temperature change.

The derivative of saturation vapour pressure with respect to temperature takes a form called the Clausius-Clapeyron equation

$$\boxed{\left(\frac{dP_e^p}{dT_0}\right)_{\mathrm{coex}} = \frac{1}{T_0}\frac{\Delta H^{p,e}}{\Delta V^{p,e}} = \frac{1}{T_0}\frac{\Delta h^{p,e}}{\Delta v^{p,e}} \qquad (6.11)}$$

where $\Delta V^{p,e} = V_g - V_l$ is the volume change in the phase transition, $\Delta v^{p,e}$ is the volume change per molecule, and $\Delta h^{p,e}$ is the latent heat per molecule. Superscript e refers to the equilibrium vapour and liquid. $\Delta h^{p,e}$ is the energy released or bound in a first-order phase transition.

The average molecular volume in the vapour is greater than in the liquid, $\Delta V^{p,e} = V_g - V_l > 0$. It can also be shown using stability conditions (p. 18) that $\Delta H^{p,e} = H_g - H_l < 0$ when l is the lower temperature phase (liquid) and g is the higher temperature phase (vapour). So the system requires energy for the vapour to evaporate, but releases energy when the vapour condenses. You can sense this, for example, when your skin is wet: you start to feel chilly because the evaporation of water takes energy from your body. In a humid sauna, when the water vapour starts to condense on your skin, you feel hot.

Latent heat $\Delta H^{p,e}$, and discontinuities in the density (or molecular volume) as well as other system properties are fingerprints of first-order phase transitions. Free energy is always continuous in the transition, but its first- or higher-order derivatives are discontinuous. Heat capacities $C_V = \left(\frac{đQ}{\partial T}\right)_{V,N}$ and $C_P = \left(\frac{đQ}{\partial T}\right)_{P,N}$ are infinite at the transition point, since heat enters/exists the system, but temperature change is zero.
Fig. 6.5 shows the behaviour of the free energy and its first derivatives in first- and second-order transitions. Table 6.1 compares the features of first-

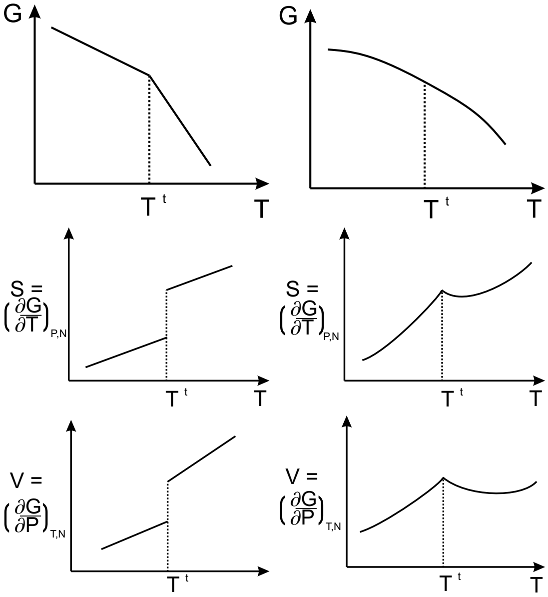

Fig. 6.5. The behaviour of the Gibbs free energy and its first derivative in a first-order (left) and second-order (right) phase transition. T^t is the phase transition temperature.

and second-order transitions. All "everyday" transitions are of first order. The standard example of a second-order transition is the transition between ferromagnetic and paramagnetic phases.

Table 6.1. Comparison of first- and second-order phase transitions.

First-order transition:	Second-order transition:
First derivatives of G are discontinuous	First derivatives of G are continuous
Nucleation	No nucleation
Latent heat	No latent heat
Second derivatives discontinuous	Second derivatives discontinuous

6.4 Second nucleation theorem

The most general form for the second nucleation theorem was (p. 122)

$$\left(\frac{\partial \Delta\varphi^*}{\partial T_0}\right)_{\mu^0_{i,g}} = -\Delta\mathcal{S}^*.$$

We want to relate this to the nucleation rate, so we need the derivative of $\Delta\varphi^*/(kT_0)$ which is inside the exponential in the expression for nucleation rate,

$$\left(\frac{\partial \frac{\Delta\varphi^*}{kT_0}}{\partial T_0}\right)_{\mu^0_{i,g}} = \frac{1}{kT_0}\left(\frac{\partial \Delta\varphi^*}{\partial T_0}\right)_{\mu^0_{i,g}} - \frac{\Delta\varphi^*}{kT_0^2} = -\frac{\Delta\mathcal{S}^*}{kT_0} - \frac{\Delta\varphi^*}{kT_0^2} = -\frac{\Delta\varphi^* + T_0\Delta\mathcal{S}^*}{kT_0^2}. \tag{6.12}$$

We use the definition of entropy change $\Delta S^* = S^*_d - \frac{V^*_l}{V^*_g}\mathcal{S}^*_g$,
formation free energy of the critical cluster
$\Delta\varphi^* = (P_0 - P^*_l)V^*_l + A^*\sigma^* = P_0V^*_l - P^*_lV^*_l + A^*\sigma^*$,
and the definition of the total volume of the system $V_{\text{tot}} = V^*_l + V^*_g$,
which can be multiplied by constant pressure P_0 to give

$$P_0V^*_l + P_0V^*_g = P_0V_{\text{tot}}. \tag{6.13}$$

Furthermore, the definition of the total number of molecules $N_{i,\text{tot}} = N^*_{i,d} + N^*_{i,g}$,
and the equality of chemical potentials in equilibrium $\mu^*_{i,l} = \mu^0_{i,g}$
can be combined to give

$$\sum N^*_{i,d}\mu^*_{i,l} + \sum N^*_{i,g}\mu^0_{i,g} - \sum N_{i,\text{tot}}\mu^0_{i,g} = 0. \tag{6.14}$$

By inserting identities (6.13) and (6.14) to the nominator of eq. (6.12) we get

$$\begin{aligned}\Delta\varphi^* + T_0\Delta S^* &= \left(-P^*_lV^*_l + A^*\sigma^* + T_0\mathcal{S}^*_d + \sum N^*_{i,d}\mu^*_{i,l}\right)\\ &\quad + \left(-P_0V^*_g + T_0\mathcal{S}^*_g + \sum N^*_{i,g}\mu^0_{i,g}\right)\\ &\quad - \left(-P_0V_{\text{tot}} + T_0\mathcal{S}^*_g\left(1 + \frac{V^*_l}{V^*_g}\right) + \sum N^*_{i,\text{tot}}\mu^0_{i,g}\right)\\ &\equiv \Delta U^*.\end{aligned} \tag{6.15}$$

In eq. (6.15) the first and second brackets represent the energy of the critical cluster plus the vapour around it, respectively, and the third brackets the energy the homogeneous vapour in volume V_{tot} would have with P_0,T_0 and $\mu^0_{i,g}$. The factor

$$\left(1 + \frac{V^*_l}{V^*_g}\right) = \frac{V^*_g + V^*_l}{V^*_g} = \frac{V_{\text{tot}}}{V^*_g}$$

scales the gas phase entropy from $\mathcal{S}^*_g$ in volume V^*_g to volume V_{tot}. Thus $\Delta U^* = \Delta\varphi^* + T_0\Delta S^*$ is the change of internal energy in the critical cluster formation:

$$\left(\frac{\partial \frac{\Delta\varphi^*}{kT_0}}{\partial T_0}\right)_{\mu^0_{i,g}} = -\frac{\Delta U^*}{kT_0^2}.$$

To link with experiments we have to convert the derivative with constant $\mu^0_{i,g}$ to a derivative with constant $\mathcal{A}_{i,g}$ or $\ln \mathcal{A}_{i,g}$. For a moment we denote

$$\frac{\Delta\varphi^*}{kT_0} = f = f\left(T_0, \mu^0_{1,g}(\mathcal{A}_{1,g}, T_0), \mu^0_{2,g}(\mathcal{A}_{2,g}, T_0), ...\right).$$

The general rule for changing variables in partial derivatives gives

$$\begin{aligned}\left(\frac{\partial f}{\partial T_0}\right)_{\mathcal{A}_{i,g}} = \left(\frac{\partial f}{\partial T_0}\right)_{\mu^0_{i,g}} &+ \left(\frac{\partial f}{\partial \mu^0_{1,g}}\right)_{T_0,\mu^0_{j,g}} \left(\frac{\partial \mu^0_{1,g}}{\partial T_0}\right)_{\mathcal{A}_{i,g}} \\ &+ \left(\frac{\partial f}{\partial \mu^0_{2,g}}\right)_{T_0,\mu^0_{j,g}} \left(\frac{\partial \mu^0_{2,g}}{\partial T_0}\right)_{\mathcal{A}_{i,g}} + ...,\end{aligned}$$

which in our case reads

$$\left(\frac{\partial f}{\partial T_0}\right)_{\mathcal{A}_{i,g}} = -\frac{\Delta U^*}{kT_0^2} - \sum_i \frac{\Delta N_i^*}{kT_0} \left(\frac{\partial \mu^0_{i,g}}{\partial T_0}\right)_{\mathcal{A}_{i,g}}, \tag{6.16}$$

where we used the first theorem $\left(\frac{\partial f}{\partial \mu^0_{i,g}}\right)_{T_0,\mu^0_{j,g}} = -\frac{\Delta N_i}{kT_0}$.

Now we still have to calculate the derivative of the chemical potential with respect to temperature $\left(\frac{\partial \mu^0_{i,g}}{\partial T_0}\right)_{\mathcal{A}_{i,g}}$.

On pages 30 and 122 we derived $\mu^0_{i,g} = \mu^p_{i,g}(P^p_{i,e}) + kT_0 \ln \mathcal{A}_{i,g}$ for the ideal mixture of ideal gases and thus

$$\left(\frac{\partial \mu^0_{i,g}}{\partial T_0}\right)_{\mathcal{A}_{i,g}} = \left(\frac{\partial \mu^p_{i,g}(P^p_{i,e})}{\partial T_0}\right) + k \ln \mathcal{A}_{i,g}. \tag{6.17}$$

To calculate $\left(\frac{\partial \mu^p_{i,g}(P^p_{i,e})}{\partial T_0}\right)$ we use the Gibbs-Duhem equation (1.9) for pure i,

$$N^p_{i,g} d\mu^p_{i,g} = V^p_{i,g} dP^p_g - \mathcal{S}^p_{i,g} dT_0$$

divide it by $N^p_{i,g}$ to get

$$d\mu^p_{i,g} = v^p_{i,g} dP^p_g - s^p_{i,g} dT_0,$$

where $v^p_{i,g}$ and $s^p_{i,g}$ are the volume and entropy per molecule in pure i vapour, and we obtain

$$\left(\frac{\partial \mu^p_{i,g}(P^p_{i,e})}{\partial T_0}\right) = v^{p,e}_{i,l} \frac{\partial P^p_{i,e}}{\partial T_0} - s^{p,e}_{i,g}.$$

But the equilibrium vapour pressure in pure vapour $P^p_{i,e}$ depends only on temperature, and partial derivatives can be converted to normal derivatives.

Thus, $\dfrac{\partial P^p_{i,e}}{\partial T_0} = \dfrac{dP^p_{i,e}}{dT_0}$ is the equilibrium vapour pressure derivative given by the Clausius-Clapeyron equation (6.11) and we get

$$\frac{\partial \mu^p_{i,g}(P^p_{i,e})}{\partial T_0} = v^{p,e}_{i,g} \frac{\varDelta h^{p,e}}{T_0 \varDelta v^{p,e}} - s^{p,e}_{i,g},$$

where the change of volume per molecule in the phase transformation is

$$\varDelta v^{p,e} = v^{p,e}_{i,g} - v^{p,e}_{i,l}$$

and the latent heat per molecule is

$$\varDelta h^{p,e} = h^{p,e}_{i,g} - h^{p,e}_{i,l}.$$

Since $v^{p,e}_{i,l} << v^{p,e}_{i,g}$, in other words molecules occupy on average much more space in gas than in liquid, we have $v^{p,e}_{i,g}/\varDelta v^e \approx 1$ and

$$\begin{aligned}\frac{\partial \mu_{i,g}(P^p_{i,e})}{\partial T_0} &= \frac{h^{p,e}_{i,g} - h^{p,e}_{i,l}}{T_0} - s^{p,e}_{i,g} \\ &= \frac{h^{p,e}_{i,g} - s^{p,e}_{i,g} T_0}{T_0} - \frac{h^{p,e}_{i,l}}{T_0}.\end{aligned}$$

For a one-component system the enthalpy reads (p. 47)

$$H = U + PV = TS + \mu N,$$

which gives for chemical potential

$$\mu = h - sT$$

and the derivative of the chemical potential can be expressed as

$$\frac{\partial \mu_{i,g}(P^p_{i,e})}{\partial T_0} = \frac{\mu^{p,e}_{i,g}}{T_0} - \frac{h^{p,e}_{i,l}}{T_0}.$$

Finally, we substitute this result and result (6.17) to eq. (6.16) and arrive at

$$\begin{aligned}\left(\frac{\partial \frac{\varDelta\varphi^*}{kT_0}}{\partial T_0}\right)_{\mathcal{A}_{i,g}} &= -\frac{\varDelta U^*}{kT_0^2} - \sum \frac{\varDelta N_i^*}{kT_0} \left(\frac{\mu^{p,e}_{i,g}}{T_0} + \frac{kT_0 \ln \mathcal{A}_{i,g}}{T_0} - \frac{h^{p,e}_{i,l}}{T_0} \right) \\ &= \frac{-\varDelta U^*}{kT_0^2} - \sum \frac{\varDelta N_i^*}{kT_0^2} \left(\mu^0_{i,g} - h^{p,e}_{i,l} \right) \qquad (6.18) \\ &= \frac{-1}{kT_0^2} \left(\varDelta U^* + \sum_i \varDelta N_i^* \left(\mu^0_{i,g} - h^{p,e}_{i,l} \right) \right).\end{aligned}$$

Now in eq. (6.15) for $\varDelta U^*$ we approximate $V_g^* \approx V_{\text{tot}}$ which means $(1 + V_l^*/V_g^*) \approx 1$ and eq. (6.15) can be written as

$$\begin{aligned}\varDelta U^* &= -P_l^* V_l^* + A^*\sigma^* + T_0\mathcal{S}_d^* + \sum N_{i,d}^*\mu_{i,l}^* + \sum\left(N_{i,g} - N_{i,\text{tot}}\right)\mu_{i,g}^0 \\ &= P_l^* V_l^* + A^*\sigma^* + T_0\mathcal{S}_d^* + \sum N_{i,d}^*\mu_{i,l}^* - \sum N_{i,d}^*\mu_{i,g}^0.\end{aligned}$$

If the liquid is much more dense than the gas we can also make the approximation

$$\varDelta N_i^* \approx N_{i,d}^*.$$

The bracketed expression in the last form of eq. (6.18) gives

$$\begin{aligned}&\varDelta U^* + \sum \varDelta N_i^*\left(\mu_{i,g}^0 - h_{i,l}^{p,e}\right) \\ &\quad= \left(-P_l^* V_l^* + A^*\sigma^* + T_0\mathcal{S}_d^* + \sum N_{i,d}^*\mu_{i,l}^*\right) - \left(\sum N_{i,d}^* h_{i,l}^{p,e}\right).\end{aligned} \tag{6.19}$$

The final approximation is that in the liquid phase the molecular enthalpy equals the molecular energy because the molecular volume is very small

$$h_{i,l}^{p,e} = u_{i,l}^{p,e} + P v_{i,l}^{p,e} \approx u_{i,l}^{p,e}$$

where energy per molecule in pure liquid is $u_{i,l}^p = \frac{U_{i,l}^p}{N_{i,l}^p}$. The term in the first brackets of eq. (6.19) is the energy of the critical cluster. The term in the second brackets can now be written as $\sum N_{i,d}^* u_{i,l}^{p,s}$, which is the energy the molecules of the cluster would have in *pure* equilibrium *liquids*. The free energy version of the second nucleation theorem finally takes the form

$$\boxed{\left(\frac{\partial \frac{\varDelta\varphi^*}{kT_0}}{\partial T_0}\right)_{\mathcal{A}_{i,g}} = -\frac{\varDelta U_{l,p}^*}{kT_0^2}.} \tag{6.20}$$

where $\varDelta U_{l,p}^*$ is defined as the difference between the energy of the cluster and the energy the molecules of the cluster would have in pure equilibrium liquids (Ford 1996).

The energy difference has three different sources:

- the pressure in the cluster is higher than in an equilibrium liquid with a flat surface
- the surface of the cluster contributes to the energy
- the molecules have different interaction energies in the mixture than in a pure liquid.

The nucleation rate is

$$J = C^* Z \exp\left(\frac{\varDelta\varphi^*}{kT_0}\right),$$

and if we neglect the derivative of the pre-exponential we get the practical form of the second nucleation theorem

$$\boxed{\left(\frac{\partial \ln J}{\partial T_0}\right)_{\mathcal{A}_{i,g}} \approx \frac{\Delta U^*_{l,p}}{kT_0^2}. \qquad (6.21)}$$

In a one-component system the contribution of the pre-exponential can be calculated explicitly to give

$$\left(\frac{\partial \ln J}{\partial T_0}\right)_{\mathcal{A}_{i,g}} = \frac{(\Delta h^{p,e})^2 - kT_0 + \Delta U^*_{l,p}}{kT_0^2}.$$

Also the second theorem can be used in two directions

1. If we have nucleation rate data as a function of temperature at constant gas phase activities (saturation ratio in one-component systems), we can calculate the internal energy of the critical cluster. Energies per molecule in pure liquid are usually known or can be calculated using tables of thermodynamic data. Remember again that the theorem is model independent, and the energy obtained is free from the assumptions of classical theory.
2. If we know the nucleation rate at one temperature and, for example from simulations, the temperature dependence of the internal energy of the critical cluster, we can integrate the second nucleation theorem and get the temperature dependence of nucleation rate.
   For one-component systems where the nucleation rate is J_0 at the saturation ratio S_0 and temperature T_0, the temperature dependence of the nucleation rate is given by

$$\ln\left(\frac{J}{J_0}\right) = \int_{T_0}^{T} \frac{\Delta U^*_{l,p}}{kT_0^2} dT.$$

Problems

6.1. Using the analytical expression for one-component nucleation rate (5.13) show that

$$\left(\frac{\partial \ln J}{\partial \ln S}\right)_{T_0} = \Delta N^* + 1$$

You have to assume $m_1 >> m^*$ and $v^* >> v_l$ to get exactly 1 for the contribution of the pre-exponential.

6.2. Experimental data (Hruby et al. J. Chem. Phys. 104, p. 5181, 1996) for nucleation rate of n-pentanol can be fitted to equation $\ln J = a - b(c/T - 1)^3/(\ln S)^2$, where the units are $[J]=1/(\mathrm{m}^3\mathrm{s})$, $[T]=\mathrm{K}$. The coefficients are $a = 68.5$, $b = 101$ and $c = 591\mathrm{K}$.

a) Calculate the expression for critical cluster size, and plot n^* as a function of saturation ratio ($7<S<20$) for T=240K and T=270K.

b) Compare the plots in a) with the classical prediction for n^*.
c) Calculate the latent heat of evaporation/condensation for n-pentanol using the Clausius-Clapeyron equation.
d) Calculate the excess energy $\Delta U^*_{l,o}$ of the critical cluster and plot the excess energy as a function of critical cluster size.

For n-pentanol the saturation vapour pressure (Pa) is
$P_e = 133.324 \exp(90.08 - 9788/T - 9.90 \ln T)$,
the surface tension is (N/m)
$\sigma = 10^{-3}[(26.85469 - 0.07889(T - 273.15\text{K})]$
and the liquid density is (mol/m^3)
$\rho_l = 10^3(3.06 + 21.90 T_r^{1/3} - 95.46 T_r^{2/3} + 218.1 T_r - 210.5 T_r^{4/3} + 74.37 T_r^{5/3})$
where $T_r = T/(588.15\text{K})$, T always in Kelvin.

7

Basics of heterogeneous nucleation

In heterogeneous nucleation the critical cluster is not formed in the middle of the vapour, but on a pre-existing surface. The surface can be provided by a microscopic pre-existing particle, also called a condensation nucleus, nucleation seed or centre, or on a planar macroscopic surface, for example a wall of the instrument. A special case of heterogeneous nucleation is ion-induced nucleation, where the cluster is formed on a charged particle or around a molecular ion (Girshick et al. 1996; Chan and Mohnen 1980; Diamond et al. 1985; Raes and Janssens 1985; Laakso et al. 2002; Yu and Turco 2000). The heterogeneous nucleation rate is higher than homogeneous nucleation rate in the same conditions: the existing surface reduces the cost of surface formation, and the nucleation barrier is lower. In the case of ion-induced nucleation the electrostatic forces enhance the interaction between the nucleation centre and the nucleating molecules, and again the nucleation barrier is lower than in homogeneous nucleation. In this book we study only a case where the pre-existing surface is electrically neutral and insoluble to the nucleating fluid, and thus we allow no exchange of molecules between the surface and vapour or liquid phases.

In classical nucleation theory the cluster is modelled as part of a sphere, and the interaction between the cluster and the underlying surface is described with a *contact angle* ϑ . ϑ is the angle between the (tangent of the) underlying surface and the tangent of the cluster surface at the point where these surfaces meet, see Figures 7.1 and 7.2. The contact angle is related to the surface tensions between liquid and solid, $\sigma_{l,\mathrm{sol}}$, vapour and liquid, $\sigma_{g,l}$, and vapour and solid $\sigma_{g,\mathrm{sol}}$ according to *Young's equation*

$$\boxed{\cos\vartheta = \frac{\sigma_{g,\mathrm{sol}} - \sigma_{l,\mathrm{sol}}}{\sigma_{g,l}}. \qquad (7.1)}$$

Since the surface of the equilibrium droplet is not moving along the solid surface, Young's equation can be derived by requiring the three surface tension related forces acting on a surface line element of length dl to balance each other in the direction parallel to the solid surface (Young 1805), or by more refined thermodynamic means (Roura and Fort 2004). Fig. 7.1 shows the mechanical force balance, each force acting parallel to the corresponding surface as in Fig. 1.5.

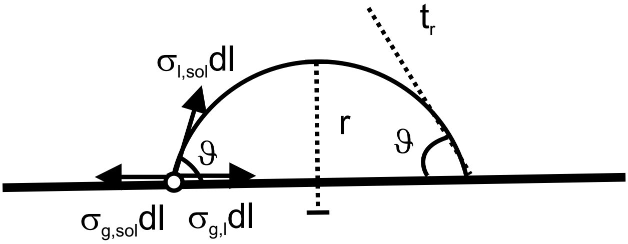

Fig. 7.1. A cluster on a planar surface. The tangent of the cluster surface is marked with t_r, r is the cluster radius and ϑ is the contact angle. Forces $\sigma_{l,\mathrm{sol}}dl$, $\sigma_{g,l}dl$, and $\sigma_{g,\mathrm{sol}}dl$ arising from surface tension between solid sol, liquid l and vapour g acting on a surface line element of length dl are also shown. The location of the surface line element (perpendicular to the page plane) is marked with a white circle.

The thermodynamics and kinetics of heterogeneous nucleation follow those of the homogeneous case; only the surface energy term and geometric relations differ.

7.1 Free energy and geometric relations

The surface contribution to the free energy (see, for example equations 3.6 and 3.29), which in the homogeneous case is $A\sigma + (\mu_{i,s} - \mu_{i,g}^0)N_{i,s}$, is in the heterogeneous case

$$\begin{aligned}\Delta\varphi_{\mathrm{surf}}^{\mathrm{het}} =& \sigma_{g,l}A_{g,l} + (\sigma_{l,\mathrm{sol}} - \sigma_{g,\mathrm{sol}})A_{l,\mathrm{sol}} + \sum_i (\mu_{i,s(g,l)} - \mu_{i,g}^0)N_{i,s(g,l)}^{\mathrm{het}} \\ &+ \sum_i (\mu_{i,s(l,\mathrm{sol})} - \mu_{i,g}^0)N_{i,s(l,\mathrm{sol})} - \sum_i (\mu_{i,s(g,\mathrm{sol})} - \mu_{i,g}^0)N_{i,s(g,\mathrm{sol})}\end{aligned} \tag{7.2}$$

$A_{g,l}$ and $A_{l,\mathrm{sol}}$ are the surface areas of the cluster (against the vapour) and the contact area between the cluster and the solid surface. When a cluster is formed, the surface between vapour and solid is replaced by a surface between solid and liquid, and an additional surface between vapour and liquid is created. We have marked the surface excess numbers and chemical potential of the gas-liquid surface by $N_{i,s(g,l)}^{\mathrm{het}}$ and $\mu_{i,s(g,l)}$, respectively. $N_{i,s(l,\mathrm{sol})}$ and

$N_{i,s(g,\mathrm{sol})}$ are the surface excess molecules related to the liquid-solid surface and same area of gas-solid surface, respectively, and $\mu_{i,s(l,\mathrm{sol})}$ and $\mu_{i,s(g,\mathrm{sol})}$ are the chemical potentials of these surface phases. The volume contribution to free energy still has the form (see eq. 3.15)

$$\Delta\varphi_{\mathrm{vol}}^{\mathrm{het}} = \sum_i \Delta\mu_i N_{i,l}^{\mathrm{het}},$$

but the relation of cluster volume V_l^{het} and thus $N_{i,d}^{\mathrm{het}}$ to the cluster radius r has to be modified compared to the homogeneous case and this relation depends also on the contact angle and the radius R_p of the pre-existing particle which is assumed spherical.

To derive expressions for the surface areas $A_{g,l}$ and $A_{l,\mathrm{sol}}$ and the volume of the cluster V_l^{het} in terms of radii r and R_p, and contact angle ϑ, we first study Fig. 7.2 (Fletcher 1958).

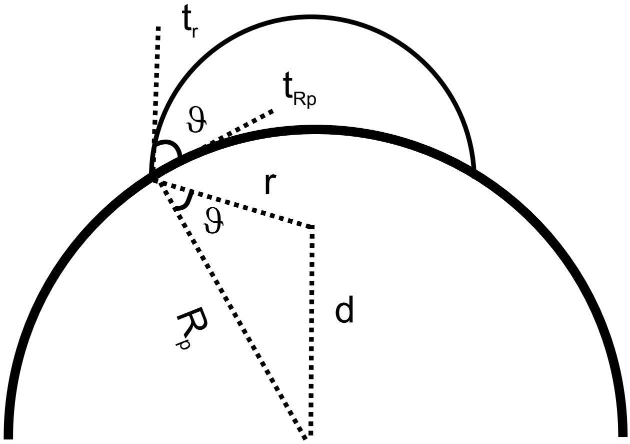

Fig. 7.2. A cluster on a surface of a spherical particle. The tangent of the cluster surface is marked with t_r, tangent of the particle surface with t_{Rp}. r is the cluster radius, R_p the particle radius and ϑ is the contact angle. The corners of the triangle shown are the centre of the spherical particle, the centre of the cluster sphere and the point where cluster and particle surfaces meet. Tangent t_r is perpendicular to the side (radius) r and tangent t_{Rp} is perpendicular to the side (radius) R_p.

Applying the cosine rule to the triangle shown in Fig. 7.2 gives the length of side d as

$$d^2 = r^2 + R_p^2 - 2rR_p\cos\vartheta = r^2(1 + X^2 - 2X\mathcal{M}) = r^2 d_X^2, \qquad (7.3)$$

where we have used dimensionless notation $X = R_p/r$, $\mathcal{M} = \cos\vartheta$ and $d_X = \sqrt{1 + X^2 - 2X\mathcal{M}}$. By dividing the triangle in Fig. 7.2 into two right-angled triangles, as shown in Fig. 7.3, we obtain the angle ϕ shown in Fig. 7.3

$$\cos\phi = \frac{R_p - r\cos\vartheta}{d} = \frac{X - \mathcal{M}}{d_X}. \tag{7.4}$$

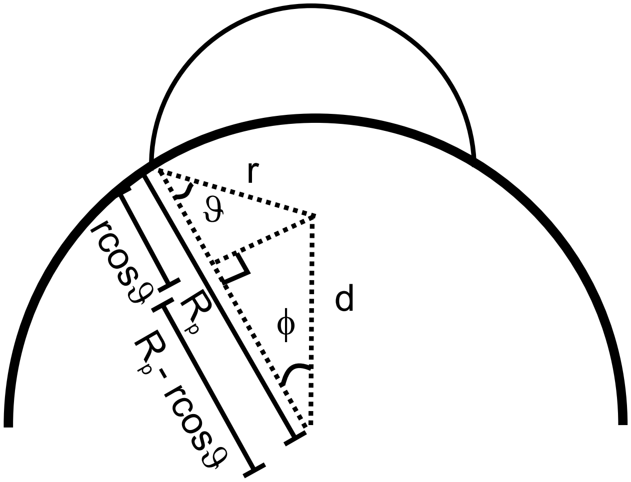

Fig. 7.3. A cluster on a surface of a spherical particle. r is the cluster radius, R_p the particle radius and ϑ is the contact angle. We have constructed right triangles to determine the angle ϕ.

Using another right-angled triangle with sides R_p, $R_p\cos\phi$ and r_{cap} we find the angle ψ in Fig. 7.4 as

$$\cos\psi = \frac{R_p\cos\phi - d}{r} = -\frac{r - R_p\cos\vartheta}{d} = \frac{-(1 - X\mathcal{M})}{d_X}, \tag{7.5}$$

where we have used equations (7.3) and (7.4) for d and $\cos\phi$, respectively.

The volume of the heterogeneous cluster is the difference in volumes (V_1 and V_2) of the caps 1 and 2 shaded in Figures 7.5 and 7.6, respectively. The surface areas $A_{g,l}$ and $A_{l,\mathrm{sol}}$ are the areas of these caps, respectively. The radius of the base of both of these caps is according to Fig. 7.4

$$r_{\mathrm{cap}} = R_p\sin\phi,$$

and the heights of the caps are according to Figures 7.5 and 7.6

$$h_1 = r(1 - \cos\psi)$$

and

$$h_2 = R_p(1 - \cos\phi).$$

The volume of the cluster is

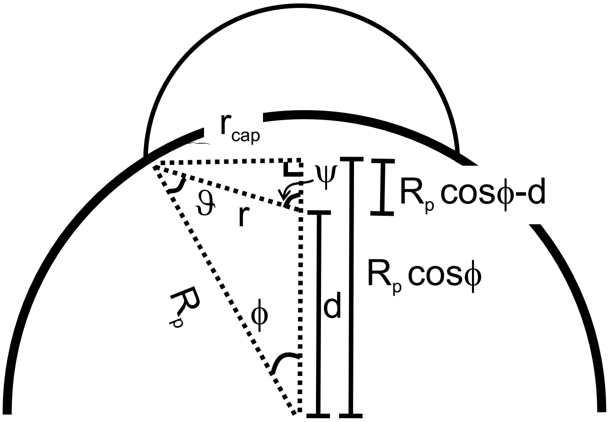

Fig. 7.4. A cluster on a surface of a spherical particle. r is the cluster radius, R_p the particle radius and ϑ is the contact angle. We have constructed right-angled triangles to determine the angle ψ and the radius of the base of the cap r_{cap}.

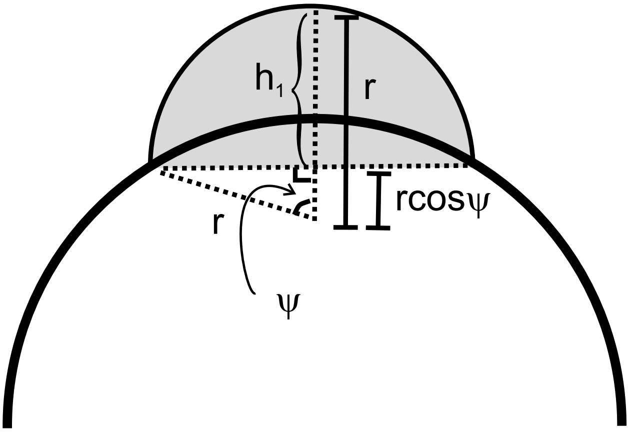

Fig. 7.5. A cluster on a surface of a spherical particle. r is the cluster radius. We have used a right-handed triangle with angle ψ and side r to determine the height h_1 of the shaded cap 1.

$$\begin{aligned} V_l^{\text{het}} =& V_1 - V_2 = \frac{\pi}{3} h_1^2 (3r - h_1) - \frac{\pi}{3} h_2^2 (3R_p - h_2) \\ =& \frac{\pi}{3} r^3 (2 - 3\cos\psi + \cos^3\psi) - \frac{\pi}{3} R_p^3 (2 - 3\cos\phi + \cos^3\phi) \end{aligned} \tag{7.6}$$

and the surface areas are given by

$$A_{g,l} = 2\pi r h_1 = 2\pi r^2 (1 - \cos\psi) \tag{7.7}$$

and

$$A_{l,\text{sol}} = 2\pi R_p h_2 = 2\pi R_p^2 (1 - \cos\phi). \tag{7.8}$$

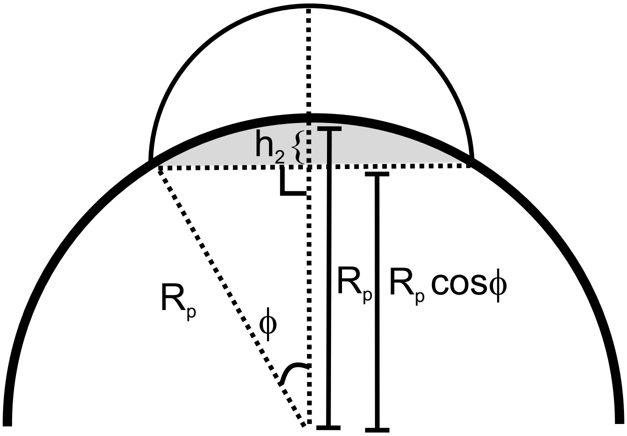

Fig. 7.6. A cluster on the surface of a spherical particle. R_p the particle radius. We have used the right-angled triangle with angle ϕ and side R_p to determine the height h_2 of the cap 2.

The length of the contact line between the cluster and the particle, needed later in the kinetic considerations, is

$$L = 2\pi r_{\text{cap}} = 2\pi R_p \sin\phi. \tag{7.9}$$

The volume of the cluster can be expressed in terms of molecular numbers, $V_l^{\text{het}} = \sum_i N_{i,l}^{\text{het}} v_{i,l}$ (see eq. 3.14), which can be solved to give the cluster radius and furthermore the surface areas needed for the surface term of the formation free energy (7.2). The critical cluster conditions are obtained by taking the derivative of the rather complicated form of free energy

$$\begin{aligned}\Delta\varphi =& \Delta\varphi_{\text{surf}}^{\text{het}} + \Delta\varphi_{\text{vol}}^{\text{het}}\\ =& \sigma_{g,l} 2\pi r^2(1-\cos\psi) + (\sigma_{l,\text{sol}} - \sigma_{g,\text{sol}})2\pi R_p^2(1-\cos\phi)\\ &+ \sum_i \Delta\mu_i N_{i,l}^{\text{het}} + (\mu_{i,s(g,l)} - \mu_{i,g}^0)N_{i,s(g,l)}^{\text{het}}\\ &+ \sum_i (\mu_{i,s(l,\text{sol})} - \mu_{i,g}^0)N_{i,s(l,\text{sol})} - \sum_i (\mu_{i,s(g,\text{sol})} - \mu_{i,g}^0)N_{i,s(g,\text{sol})}\end{aligned} \tag{7.10}$$

with respect to bulk and surface excess numbers of molecules of each component at a time. We use the Gibbs-Duhem equation (1.9) for bulk liquid and the Gibbs adsorption isotherm (1.12) for gas-liquid, gas-solid and solid-liquid surfaces to get rid of the derivatives of all chemical potentials and surface tensions. It must be kept in mind that angles ψ and ϕ depend on cluster radius and thus number of molecules in the cluster. Taking the complicated derivatives of eq. (7.10) is not necessary, since the equilibrium conditions turn out to be the same as in the homogeneous case, in other words the Kelvin equation (2.15)

$$\Delta\mu_i + \frac{2\sigma_{g,l} v_{i,l}}{r^*} = 0$$

is valid also in the heterogeneous case. This is a natural result, as the liquid under the curved surface of the droplet has to be in equilibrium with the vapour above the surface irrespective of the fact that the cluster is attached to a pre-existing surface. Also the chemical potentials in all phases must be equal in equilibrium

$$\mu_{i,s(g,l)} = \mu_{i,s(g,\mathrm{sol})} = \mu_{i,s(l,\mathrm{sol})} = \mu_{i,l} = \mu_{i,g}^0 .$$

Thus, the composition and radius of the heterogeneous critical cluster are the same as in homogeneous nucleation at the same temperature and vapour concentrations.

The number of molecules in a homogeneous critical cluster at the same conditions is given by

$$N_{i,l}^{\mathrm{hom}*} = x_{i,l}^* \frac{4\pi}{3} r^{*3} \rho_l(x_{i,l}^*, T_0),$$

the number of molecules in the heterogeneous cluster is

$$N_{i,l}^{\mathrm{het}*} = f_V N_{i,l}^{\mathrm{hom}*},$$

where the geometric factor relating heterogeneous cluster volume, and thus also number of bulk molecules, to the homogeneous case, $f_V = V_l^{*\mathrm{het}}/V_l^{*\mathrm{hom}} = N_{i,l}^{\mathrm{het}}/N_{i,l}^{\mathrm{hom}}$, can be written as

$$\begin{aligned} f_V =& \frac{1}{4}\left\{2 + 3\left(\frac{1 - X\mathcal{M}}{d_X}\right) - \left(\frac{1 - X\mathcal{M}}{d_x}\right)^3 \right. \\ & \left. -X^3\left[2 - 3\left(\frac{X - \mathcal{M}}{d_X}\right) + \left(\frac{X - \mathcal{M}}{d_X}\right)^3\right]\right\}. \end{aligned} \tag{7.11}$$

Surface excess numbers related to the gas-liquid surface can be solved in the same way as in the homogeneous case on p. 70. The set of equations to solve is (3.25) and (3.26) with $j = 1, ...n - 1$. The area A in eq. (3.26) is in the heterogeneous case the area of gas-liquid surface $A_{g,l} = 2\pi r^2(1 - \cos\vartheta)$, and the chemical potential differentials needed are given by eq. (3.27), as in the homogeneous case.

In equilibrium, the formation energy of the critical cluster becomes

$$\begin{aligned}\Delta\varphi^{\mathrm{het}*} =& \sum_i \Delta\mu_i N_{i,d}^{\mathrm{het}*} + \sigma_{g,l} A_{g,l}^{*} + (\sigma_{g,\mathrm{sol}} - \sigma_{l,\mathrm{sol}}) A_{l,\mathrm{sol}}^{*} \\ =& \sum_i \Delta\mu_i N_{i,d}^{\mathrm{het}*} + \sigma_{g,l} A_{g,l}^{*} - \cos\vartheta \sigma_{g,l} A_{l,\mathrm{sol}}^{*},\end{aligned}$$

where we have used Young's equation (7.1) to express the surface tensions $\sigma_{g,\mathrm{sol}}$ and $\sigma_{l,\mathrm{sol}}$ in terms of contact angle and surface tension $\sigma_{g,l}$. Using Kelvin equations (2.15) for the chemical potential differences we get

$$\begin{aligned}\Delta\varphi^{\mathrm{het}*} =& -\sum_i N_{i,d}^{\mathrm{het}*} v_{i,l} \frac{2\sigma_{g,l}^{*}}{r^*} + \sigma_{g,l}^{*} A_{g,l}^{*} + \cos\vartheta \sigma_{g,l}^{*} A_{l,\mathrm{sol}}^{*} \\ =& \sigma_{g,l}^{*} \left(\frac{-2V_l^{\mathrm{het}*}}{r^*} + A_{g,l}^{*} - \cos\vartheta A_{l,\mathrm{sol}}^{*} \right),\end{aligned} \tag{7.12}$$

where we have used the equimolar surface result (3.14) to convert $\sum_i N_{i,d}^{\mathrm{het}*} v_{i,l}$ to cluster volume.

Substitution of expressions (7.6), (7.7) and (7.8), for the volume V_l, area A_{gl}^{*} and area A_{ls}^{*}, respectively, to eq. (7.12) gives

$$\begin{aligned}\Delta\varphi^{\mathrm{het}*} =& \frac{2\pi r^2 \sigma_{g,l}}{3} \left[1 - \cos^3\psi + \left(\frac{R_p}{r}\right)^3 (2 - 3\cos\phi + \cos\phi^3) \right. \\ & \left. -3\cos\vartheta \left(\frac{R_p}{r}\right)^2 (1 - \cos\phi) \right],\end{aligned}$$

which can be written as

$$\Delta\varphi^{\mathrm{het}*} = f_\varphi \frac{4\pi r^{*2} \sigma_{g,l}}{3} = f_\varphi \Delta\varphi^{\mathrm{hom}*}, \tag{7.13}$$

where $\Delta\varphi^{\mathrm{hom}*}$ is the formation free energy of the homogeneous critical cluster at the same conditions, and the geometric factor f_φ can be written in terms of the ratio of radii $X = r^*/R_p$ and cosine of the contact angle $\mathcal{M}$ as

$$\begin{aligned}f_\varphi =& \frac{1}{2} \left\{ 1 + \left(\frac{1 - X\mathcal{M}}{d_X}\right)^3 + X^3 \left[1 - 3\left(\frac{X - \mathcal{M}}{d_X}\right) + \left(\frac{X - \mathcal{M}}{d_X}\right)^3 \right] \right. \\ & \left. +3\mathcal{M}X^2 \left(\frac{X - \mathcal{M}}{d_X} - 1 \right) \right\}.\end{aligned} \tag{7.14}$$

For all values of X and $\mathcal{M}$ the geometric factor is lower than one, $0 < f_\varphi \leq 1$, reflecting the fact that in heterogeneous nucleation the energetic barrier is lower than in homogeneous nucleation as shown in Fig. 7.7. Note that the location of the maximum in the curve showing the formation free energy as a function of the cluster radius is the same in both heterogeneous and homogeneous cases, reflecting the fact that the critical radii are the same. However, the number of molecules in the critical cluster is smaller in the heterogeneous case by a factor of f_V. Heterogeneous nucleation occurs at much lower vapour concentrations than homogeneous nucleation, typically soon after saturation ratio exceeds 1. The homogeneous case, $f_\varphi = f_V = 1$, is obtained by setting $X = 0$ ($R_p = 0$) or $\mathcal{M} = -1$ (contact angle π or 180°).

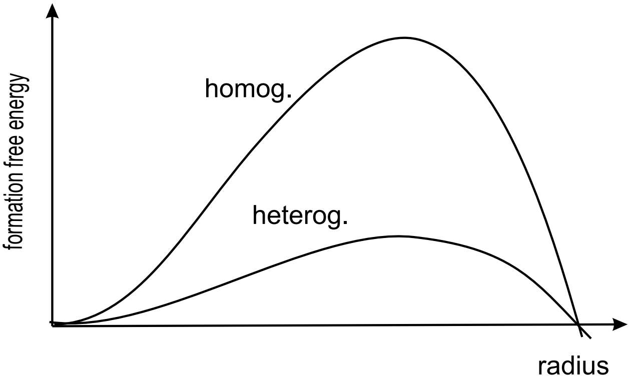

Fig. 7.7. Formation free energy of a cluster as a function of the cluster radius in homogeneous and heterogeneous cases.

7.1.1 Flat pre-existing surface

The geometric relations simplify considerably if the nucleus forms on a planar surface. Fig. 7.8 shows that the height of the cap can now be written as

$$h = r(1 - \cos\vartheta)$$

and the radius of the base of the cap is

$$r_{\mathrm{cap}} = r\sin\vartheta.$$

The volume of the cap is now

$$V_l^{\mathrm{het}} = \frac{\pi}{3}h^2(3r - h) = \frac{\pi r^3}{3}(2 - 3\cos\vartheta + \cos^3\vartheta),$$

and the surface area of the cap is

$$A_{g,l} = 2\pi r h = 2\pi r^2(1 - \cos\vartheta)$$

the area of the liquid-solid surface is

$$A_{l,\mathrm{sol}} = \pi r_{\mathrm{cap}}^2 = \pi r^2 \sin^2\vartheta,$$

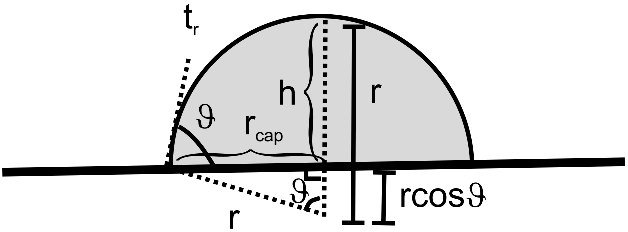

Fig. 7.8. A cluster on a planar surface. r is the cluster radius, and ϑ is the contact angle. The left-hand side (radius r) of angle ϑ in the right-angled triangle is perpendicular to the tangent of the cluster surface t_r, and the right-hand side that angle (vertical line) is perpendicular to the pre-existing surface, and thus this angle is the same as the contact angle between the planar surface and the tangent of the cluster surface.

and the length of the contact line is

$$L = 2\pi r_{\text{cap}} = 2\pi r \sin\vartheta.$$

Substituting these to eq. (7.12) shows that the geometric factor for free energy equals that for the volume in the flat condensation surface case,

$$f_\varphi = f_V = \frac{1}{4}\left(2 - 3\cos\vartheta + \cos^3\vartheta\right) = \frac{1}{4}\left(2 - 3\mathcal{M} + \mathcal{M}^3\right).$$

This result can also be obtained from the general expressions (7.11) and (7.14) at the limit $X = R_p/r \to \infty$.

7.2 Nucleation rate

The analysis leading to a general expression for the nucleation rate (eq. 5.27) is valid also in the heterogeneous case, and the heterogeneous nucleation rate can be written as

$$\boxed{J_{\text{het}} = \frac{|\lambda_1^{\text{het}}|}{2\pi kT_0} F_{\text{het}}^e \exp\left(\frac{-\Delta\varphi^{\text{het}*}}{kT_0}\right) \frac{1}{\sqrt{\left|\det\left(\frac{\underline{W}^*_{\text{het}}}{2\pi kT_0}\right)\right|}}. \qquad (7.15)}$$

The components of matrix $\underline{W}^*_{\text{het}}$ are the second derivatives of the heterogeneous formation free energy (7.10) with respect to the numbers of molecules $N_{i,d}^{\text{het}}$ in the cluster, and λ_1^{het} is the negative eigenvalue of of product matrix $\underline{R}^*_{\text{het}}\underline{W}^*_{\text{het}}$. $\underline{R}^*_{\text{het}}$ is the heterogeneous growth matrix, whose components give the rate at which monomers of different types collide with the critical cluster.

F^{e}_{het} is the normalization factor in the cluster size distribution. In the heterogeneous case the cluster distribution in question is the distribution of different cluster sizes on the pre-existing particle surfaces, and as in the homogeneous case it can be approximated by the sum of monomer concentrations on the surfaces of pre-existing particles in the equilibrium vapour $F^{e}_{\mathrm{het}} = \sum_i C^{e,\mathrm{het}}_{i,\mathrm{mon}}$.

7.2.1 Concentration of adsorbed monomers

The monomer concentration on the pre-existing particle surfaces can be estimated using various methods. The simplest approach is to assume that the condensation nuclei are covered with a monolayer (Inada 2002) of condensing molecules. The thickness of the monolayer is the diameter of an average monomer (see also p. 113), $2r_x$, where $4\pi r_x^3/3 = \sum x_{i,g} v^{o}_{i,l}$ is the average volume of a monomer. We have assumed that the mole fractions of different components on the surface are the same as in the gas phase. The monolayer approach gives for a number of adsorbed particles per unit area

$$C^{e,\mathrm{het}}_{i,\mathrm{mon}} = x_{i,g} \frac{2r_x}{v_x}. \tag{7.16}$$

This is a very crude approximation, but gives an upper limit for the concentration of adsorbed monomers.

The equilibrium concentration for adsorbed monomers can also be calculated by balancing the flux of molecules hitting the particle surfaces with the flux of particles escaping the surface. According to kinetic gas theory the incoming monomer flux per unit area is

$$C^{e,\mathrm{vapour}}_{i,\mathrm{mon}} \sqrt{\frac{kT_0}{2\pi m_i}}, \tag{7.17}$$

where $C^{e,\mathrm{vapour}}_{i,\mathrm{mon}}$ is the concentration of monomers in the equilibrium vapour. The outgoing desorption flux per unit area is

$$C^{e,\mathrm{het}}_{i,\mathrm{mon}} \nu_{i,\mathrm{des}} \exp\left[\frac{-\Delta e_{i,\mathrm{des}}}{kT_0}\right], \tag{7.18}$$

where $\nu_{i,\mathrm{des}}$ is the frequency of vibration of the adsorbed molecule on the substrate, and $\Delta e_{i,\mathrm{des}}$ is the adsorption/desorption energy per molecule (Pruppacher and Klett 1997). Equating (7.17) with (7.18) gives the number of adsorbed molecules per unit area as

$$C^{e,\mathrm{het}}_{i,\mathrm{mon}} = C^{e,\mathrm{vapour}}_{i,\mathrm{mon}} \sqrt{\frac{kT_0}{2\pi m_i}} \frac{1}{\nu_{i,\mathrm{des}}} \exp\left[\frac{\Delta e_{i,\mathrm{des}}}{kT_0}\right]. \tag{7.19}$$

7.2.2 Growth coefficients

If we assume the growth of the critical cluster to occur by vapour molecules hitting the cap surface, the growth coefficients β_i^{het} (unit 1/s) (components of matrix $\underline{R}^*_{\text{het}}$) are given by the monomer flux per unit area (7.17) times the area of the cap (7.7),

$$\beta_i^{\text{het}} = C_{i,\text{mon}}^{e,\text{vapour}} \sqrt{\frac{kT_0}{2\pi m_i}} 2\pi r^{*2}(1-\cos\psi^*). \tag{7.20}$$

This approach is called the direct vapour deposition model (Pruppacher and Klett 1997; Inada 2002).

In the surface diffusion approach, the critical cluster grows when monomers adsorbed on the pre-existing particle diffuse along the particle surface into the cluster. If the adsorbed molecules jump on average a distance δ_i, molecules in a circular band of length L^* and width δ_i around the cluster are in position to join the cluster. Here L^* is the length of the contact line between the surface and the cluster given by (7.9). The number of molecules in that band is $C_{i,\text{mon}}^{e,\text{het}} L^* \delta_i = C_{i,\text{mon}}^{e,\text{het}} \delta_i 2\pi R_p \sin\phi^*$. If $\nu_{i,\text{diff}}$ is the frequency related to vibrations leading to diffusion jumps and $\Delta e_{i,\text{diff}}$ is the activation energy for surface diffusion, the frequency of diffusion jumps is $\nu_{i,\text{diff}} \exp[-\Delta e_{i,\text{diff}}/(kT_0)]$ and the growth coefficient (1/s) is

$$\beta_i^{\text{het}} = C_{i,\text{mon}}^{e,\text{het}} \delta_i 2\pi R_p \sin\phi^* \nu_{i,\text{diff}} \exp\left[\frac{-\Delta e_{i,\text{diff}}}{kT_0}\right]. \tag{7.21}$$

In reality, both surface diffusion and direct vapour deposition are working at the same time. The growth rate due to direct vapour deposition is however typically orders of magnitude smaller than the rate of surface diffusion, and thus it is enough to use the surface diffusion growth coefficients.

7.2.3 Units of nucleation rate and nucleation probability

The growth coefficients (7.20) and (7.21) have units 1/s, and the eigenvalue λ_1^{het} has units J/s as in the homogeneous case. F^e in eq. (7.15) has units of $C_{i,\text{mon}}^{e,\text{het}}$, namely 1/m^2. Thus the unit of heterogeneous nucleation rate given by eq. (7.15) is 1/(m^{2}s) – the number of critical clusters formed per unit area of pre-existing surface per second. If we want the number of critical clusters formed per time and volume unit, we have to multiply J_{het} of eq. (7.15) by the number concentration of pre-existing particles (1/m^3) and the surface area of one such particle, $4\pi R_p^2$. We can also express the nucleation rate as the number of critical clusters formed per condensation nucleus per unit time, in which case we have to multiply J_{het} of eq. (7.15) by $4\pi R_p^2$.

The quantity that is most often measured in heterogeneous nucleation is nucleation probability P, which is the probability that one critical cluster forms on a pre-existing condensation nucleus in a chosen (experimental) time period t. Using our notation (7.15) for nucleation rate, the nucleation probability is given by

$$\boxed{P = 1 - \exp(-J_{\mathrm{het}} 4\pi R_p^2 t). \qquad (7.22)}$$

Fig. 7.9 shows that the nucleation probability as a function of saturation ratio resembles a step function, which rises from zero to one soon after the saturation ratio exceeds 1.

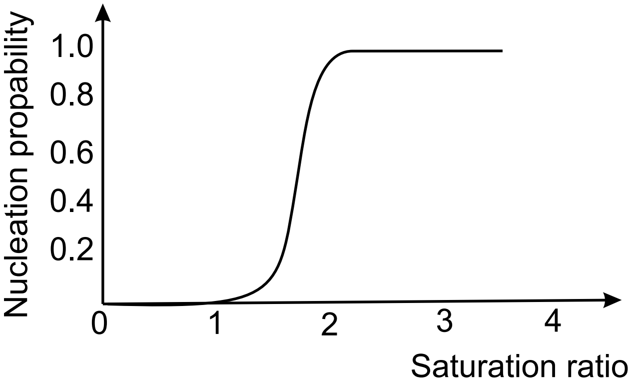

Fig. 7.9. One-component nucleation probability as a function of saturation ratio of the nucleating vapour.

7.2.4 One-component case

In the one-component case, the heterogeneous nucleation rate can be written as

$$\boxed{J_{\mathrm{het}} = \beta^{\mathrm{het}*} C_{\mathrm{mon}}^{e,\mathrm{het}} \exp\left(\frac{-\Delta\varphi^{\mathrm{het}*}}{kT_0}\right) Z_{\mathrm{het}}, \qquad (7.23)}$$

where the growth coefficient $\beta^{\mathrm{het}*}$ is given by either eq. (7.20) or eq. (7.21), the number of adsorbed monomers $C_{\mathrm{mon}}^{\mathrm{e,het}}$ is given by either eq. (7.19) or eq. (7.16), and the formation free energy $\Delta\varphi^{\mathrm{het}*}$ is obtained from the homogeneous formation free energy at the same temperature and saturation ratio by multiplying with the geometric factor f_φ given by eq. (7.14).

As in the homogeneous case (see p. 94), the Zeldovich factor is defined as

$$Z_{\mathrm{het}} = \sqrt{\frac{-1}{2\pi k T_0} \left(\frac{\partial^2 \Delta\varphi^{\mathrm{het}}}{\partial (N_d^{\mathrm{het}})^2} \right)^*}.$$

To obtain an explicit form for the Zeldovich factor we have to take the second derivative of formation free energy (7.10) in the one-component case. We use the equimolar surface condition $N_s = 0$, which means $N_d^{\text{het}} = N_l^{\text{het}}$, and the volume term is simply

$$\varDelta\varphi_{\text{vol}}^{\text{het}} = \varDelta\mu N_d^{\text{het}},$$

and the first derivative of the volume term gives

$$\frac{\partial \varDelta\varphi_{\text{vol}}^{\text{het}}}{\partial N_d} = \varDelta\mu.$$

Using equations (7.3), (7.4) and (7.5) for d and angles ϕ and ψ, respectively, the surface term can be written as

$$\varDelta\varphi_{\text{surf}}^{\text{het}} = 2\pi\sigma_{g,l}\left(r^2 - \mathcal{M}R_p^2 + \frac{r^3 - r^2R_p\mathcal{M} - rR_p^2\mathcal{M}^2 + R_p^3\mathcal{M}}{\sqrt{r^2 - 2rR_p\mathcal{M} + R_p^2}}\right). \tag{7.24}$$

The derivative is easiest to take using the chain rule

$$\frac{\partial \varDelta\varphi_{\text{surf}}^{\text{het}}}{\partial N_d} = \left(\frac{\partial \varDelta\varphi_{\text{surf}}^{\text{het}}}{\partial r}\right)\left(\frac{\partial r}{\partial N_d^{\text{het}}}\right) = \left(\frac{\partial \varDelta\varphi_{\text{surf}}^{\text{het}}}{\partial r}\right)\left(\frac{\partial N_d^{\text{het}}}{\partial r}\right)^{-1}. \tag{7.25}$$

Thus we also need the dependence of the number of molecules on the radius given by $N_d^{\text{het}} = V_l^{\text{het}}/v_l$, which, using again equations (7.3),(7.4) and (7.5) in formula (7.6) for the cluster volume, gives (after reduction)

$$\begin{aligned} N_d^{\text{het}} =& \frac{\pi}{3v_l}\Bigg(2r^3 - 2R_p^3 \\ &+ \frac{2r^4 - 2r^3R_p\mathcal{M} - r^2R_p^2(\mathcal{M}^2 - 1) - 2rR_p^3\mathcal{M} + 2R_p^4}{\sqrt{r^2 - 2rR_p\mathcal{M} + R_p^2}}\Bigg) \end{aligned} \tag{7.26}$$

The derivatives of equations (7.25) and (7.26) with respect to r written in terms of the dimensionless parameter X are

$$\frac{\partial \varDelta\varphi_{\text{surf}}^{\text{het}}}{\partial r} = 2\pi r\sigma_{g,l}\left\{2 + \frac{(1 - \mathcal{M}X)[2 - 4\mathcal{M}X - (\mathcal{M}^2 - 3)X^2]}{(1 - 2\mathcal{M}X + X^2)^{3/2}}\right\}$$

and

$$\frac{\partial N_d^{\text{het}}}{\partial r} = \frac{\pi r^2}{v_l}\left\{2 + \frac{(1 - \mathcal{M}X)[2 - 4\mathcal{M}X - (\mathcal{M}^2 - 3)X^2]}{(1 - 2\mathcal{M}X + X^2)^{3/2}}\right\}.$$

The first derivative of the formation free energy is

$$\frac{\partial \Delta\varphi^{\mathrm{het}}}{\partial N_d^{\mathrm{het}}} = \frac{\partial \Delta\varphi_{\mathrm{vol}}^{\mathrm{het}}}{\partial N_d^{\mathrm{het}}} + \frac{\partial \Delta\varphi_{\mathrm{surf}}^{\mathrm{het}}}{\partial r}\left(\frac{\partial N_d^{\mathrm{het}}}{\partial r}\right)^{-1} = \Delta\mu + \frac{2\sigma_{g,l}v_l}{r},$$

which explicitly confirms that (in the one-component case) the Kelvin equation is obtained by setting the first derivative of the formation free energy to zero. The second derivative is then

$$\begin{aligned}\left(\frac{\partial^2 \Delta\varphi^{\mathrm{het}}}{\partial (N_d^{\mathrm{het}})^2}\right) =& \frac{-2\sigma_{g,l}v_l}{r^2}\left(\frac{\partial r}{\partial N_d^{\mathrm{het}}}\right) = \frac{-2\sigma_{g,l}v_l}{r^2}\left(\frac{\partial N_d^{\mathrm{het}}}{\partial r}\right)^{-1}\\ =& \frac{-2\sigma_{g,l}v_l^2}{\pi r^4}\left[\frac{1}{2+\frac{(1-\mathcal{M}X)[2-4\mathcal{M}X-(\mathcal{M}^2-3)X^2]}{(1-2\mathcal{M}X+X^2)^{3/2}}}\right],\end{aligned}$$

and the Zeldovich factor has the form

$$\begin{aligned}Z_{\mathrm{het}} =& \frac{v_l}{\pi r^{*2}}\sqrt{\frac{\sigma_{g,l}}{kT_0}}\sqrt{\frac{1}{2+\frac{(1-\mathcal{M}X^*)[2-4\mathcal{M}X^*-(\mathcal{M}^2-3)X^{*2}]}{(1-2\mathcal{M}X^*+X^{*2})^{3/2}}}}\\ =& Z_{\mathrm{hom}}\sqrt{\frac{4}{2+\frac{(1-\mathcal{M}X^*)[2-4\mathcal{M}X^*-(\mathcal{M}^2-3)X^{*2}]}{(1-2\mathcal{M}X^*+X^{*2})^{3/2}}}}.\end{aligned}$$

Z_{het} reduces to $Z_{\mathrm{hom}} = v_l/(2\pi r^{*2})\sqrt{\sigma_{g,l}/(kT_0)}$ when $\mathcal{M} = -1$ or $X^* = 0$, as it should.

7.3 Heterogeneous nucleation theorems

Nucleation theorems are valid also for the heterogeneous case, and the free energy versions read (Kashchiev 2000)

$$\left(\frac{\partial \frac{\Delta\varphi^{\mathrm{het}*}}{kT_0}}{\partial \ln \mathcal{A}_{i,g}}\right)_{\mathcal{A}_{j,g},T_0} = -\left(N_{i,d}^{\mathrm{het}*} - V_l^{\mathrm{het}*}\frac{N_{i,g}^{\mathrm{het}*}}{V_g^{\mathrm{het}*}} + N_{i,s(l,\mathrm{sol})} - N_{i,s(g,\mathrm{sol})}\right)$$

and

$$\left(\frac{\partial \frac{\Delta\varphi^{\mathrm{het}*}}{kT_0}}{\partial T_0}\right)_{\mathcal{A}_{i,g}} = -\left(\frac{\Delta U_{l,p}^{\mathrm{het}*} + \Delta U_{l,\mathrm{sol},p} - \Delta U_{g,\mathrm{sol},p}}{kT_0^2}\right),$$

where $\Delta U_{l,\mathrm{sol},p}$ is the energy differences of molecules on the liquid-solid interface compared to the same molecules in the pure bulk liquid. $\Delta U_{g,\mathrm{sol},p}$ is the energy difference between molecules on the area $A_{l,\mathrm{sol}}$ of gas-solid interface compared to the same molecules in pure bulk liquids.

The contribution of the kinetic pre-factor to $(\partial \ln J_{\text{het}}/\partial \ln \mathcal{A}_{i,g})_{\mathcal{A}_{j,g},T_0}$ and $(\partial \ln J_{\text{het}}/\partial T_0)_{\mathcal{A}_{i,g}}$ is small also in the heterogeneous case. The exact value of the contribution of the pre-factor depends on which model is used for growth and concentration of adsorbed molecules.

The nucleation theorems can be explicitly derived for classical heterogeneous formation energy by taking a derivative of eq. (7.13), which involves the derivative of homogeneous formation free energy and geometrical pre-factor f_φ and using the homogeneous nucleation theorems. Young's equation (7.1) is used to express contact angle in terms of surface tensions, and we also use the Gibbs-Duhem equation (1.9) for bulk liquid and the Gibbs adsorption isotherm (1.12) for gas-liquid, gas-solid and solid-liquid interfaces. The heterogeneous nucleation theorems can also be derived with less algebraic manipulation starting from a more general expression for the formation as we did in the homogeneous case on p. 119. In the heterogeneous case the critical cluster surface energy $\sigma^* A^*$ must be replaced by $\sigma^*_{g,l}A^*_{g,l} + (\sigma^*_{l,\text{sol}} - \sigma^*_{g,\text{sol}})A^*_{l,\text{sol}}$.

Problems

7.1. Plot the formation free energy of homogeneous and heterogeneous water clusters on planar glass surface as a function of
a) number of molecules
b) radius
of the cluster at saturation ratio 5 and temperature is 298.15K.
Contact angle for water on steel is 14°.

The saturation vapour pressure of water is (T in Kelvin)
$P_e = \exp[77.34 - 7235.42/T - 8.2\ln(T) + 0.00571T]$ Pa.
Density of liquid water is
$\rho_l = (1049.572 - 0.1763T)$ kg/m^3.
Molar mass of water is 18.02 g/mol.
Surface tension of pure water is
$\sigma = (0.117 - 0.152 \cdot 10^{-3}T\ )$ N/m.
Water vapour is assumed to be an ideal gas, and liquid is assumed incompressible.

7.2. Plot the formation free energy of homogeneous and heterogeneous critical clusters as a function of pre-existing particle radius. The clusters consist of water, and the pre-existing particles are made of steel. Saturation ratio is 4 and temperature is 273.15K.
Contact angle for water on steel is 75°.

The saturation vapour pressure of water is (T in Kelvin)
$P_e = \exp[77.34 - 7235.42/T - 8.2\ln(T) + 0.00571T]$ Pa.
Density of liquid water is

$\rho_l = (1049.572 - 0.1763T)$ kg/m^3.
Molar mass of water is 18.02 g/mol.
Surface tension of pure water is
$\sigma = (0.117 - 0.152 \cdot 10^{-3} T\ )$ N/m.
Water vapour is assumed to be an ideal gas, and liquid is assumed incompressible.

7.3. Plot the geometric factors for volume (f_V)and free energy (f_φ), ratio of gas-liquid surface areas $A_{g,l,\mathrm{het}}/A_{\mathrm{hom}}$, and the ratio of one-component Zeldovich factors $Z_{\mathrm{het}}/Z_{\mathrm{hom}}$ as a function of
a) ratio of radii $X^* = R_p/r^*$ with constant contact angles 10°, 70° and 110°.
b) contact angle with $X^* = 1$, $X^* = 100$ and $X^* = 10^6$.

8

Beyond the classical theory

8.1 Improved classical theories

Several improvements to the basic classical theory have been suggested. The motivation for some of the improvements is to get rid of the theoretical inconsistencies (p. 74) of the classical theory (Girshick and Chiu 1990; Girshick 1991; Courtney 1961; Blander and Katz 1972), like the non-zero formation energy of a single vapour molecule. The consistency requirements involve also the normalisation factor (F^e, see p. 82) in the cluster distribution (Wilemski and Wyslouzil 1995). Another motivation is to incorporate physical phenomena that are not properly included in the original version of the classical theory, such as curvature dependence of the surface tension, the contribution of the translational and rotational degrees of freedom to the free energy (Lothe and Pound 1962; Reiss et al. 1968; Dillmann and Meier 1989, 1991; Ford et al. 1993; Delale and Meier 1993; Kalikmanov and van Dongen 1993a,b) and surface segregation (Flageollet-Daniel et al. 1983; Laaksonen 1992). In general, the self-consistent theories succeed no better in predicting observed nucleation rates than does the classical theory. However, models that incorporate surface enrichment in binary systems give reasonable values in cases where the original classical theory gives unphysical results. Often the improved theories predict the rates well for some substances and conditions, but fail in other cases, just like the original classical theory.

8.2 Scaling theories

In Hale's scaling model (Hale 1986), the density and the surface tension of one-component clusters are assumed to depend only on the reduced temperature T/T_c (T_c is the temperature at the critical point) and properties of the liquid at the critical point, and some material-dependent empirical constants. The formation energy is calculated using the classical formula. The theories give dimensionless forms for the temperature dependence of nucleation rate and critical saturation ratio. Another form of scaling model (McGraw 1981) is obtained by assuming that the ratio $\frac{\Delta\varphi}{n^*\Delta\mu}$ differs from its classical value of 1/2 by a correction function which depends on n^* and $\Delta\mu$. By using the first nucleation theorem and some simplifying assumptions this can be shown to lead to the conclusion that real formation free energy and classical formation free energy differ by a semi-empirical function that depends only on temperature. The scaling models predict the value of onset saturation ratio well in many cases where the original form of the classical theory fails.

8.3 The density functional theory

The density functional theory is based on statistical mechanics, and allows the use of realistic molecular interactions instead of macroscopic properties of matter (Evans 1979; Zeng and Oxtoby 1991b,a; Henderson 1992). Surface enrichment and curvature effects are naturally taken into account in this theory. The nucleating system is treated as an inhomogeneous fluid, where the average density of molecules varies with the position in space. The free energy is a non-local functional of the density function. The density profile and the formation free energy are obtained by searching for the point in the function space at which the functional derivative of the free energy with respect to the density vanishes. Some attempts have been made to use the concepts of the density functional theory and calculate directly the nucleation rate, not only the formation energy, of the critical cluster (Langer and Turski 1973; Talanquer and Oxtoby 1995). The numerical solution of density functional theory gets complicated if the cluster is not spherically symmetric, and thus most of the systems studied are simplified model systems that describe some features of real systems. Potentials describing, for example, real water lead to a situation where the spherical symmetry of the cluster is broken, and computational costs increase beyond practical use. Researchers have developed suitable symmetric potentials that describe to some extent hydrogen bound, polar and asymmetric molecules and used them in density functional studies (Talanquer and Oxtoby 1993; Oxtoby and Evans 1988). Seok and Oxtoby (1998) have used density functional theory to study alkanes and Napari *et al.* (2000) have studied a model system imitating a surface-active water-ethanol mixture. Agreement with experimental nucleation rate is qualitatively good for several systems. Especially the temperature dependence of the nucleation rate, which is inaccurate in the classical theory, is clearly improved. In binary systems, measurable deviations from the classical theory can be seen in Lennard-Jones mixtures that mimic systems with surface segregation (Laaksonen and Oxtoby 1995). The density functional theory gives reasonable results even in situations where the predictions of the classical theory are unphysical.

8.4 The diffuse interface theory

In the diffuse interface theory, the formation energy is evaluated in terms of a characteristic interface thickness. The characteristic thickness is related to properties of bulk liquid, namely the volumetric heat of evaporation and the surface tension of planar surface. This theory gives a curvature correction to the surface tension up to second order in terms of the characteristic thickness. The nucleation formulae are quite simple, and the level of approximation is between the classical theory and the density functional theory. For several systems the agreement is better than with classical theory, but for some others, for example pure water, the predictions are poorer than those of classical theory (Granasy 1993, 1996).

8.5 Molecular simulations

Here, we mean by simulations computer algorithms that mimic – "simulate" – the movement of molecules in time or the sequence of molecular configurations statistically likely in nature. In these methods the description of clusters starts from the location of individual molecules and atoms within them, in the case of quantum mechanical methods even electrons, rather than some average position-related quantity like molecular density. This short description of nucleation-related computer simulations is modified from an extended review abstract (Vehkamäki 2004).

8.5.1 Interaction potentials

Choosing a realistic interaction potential is the starting point of any realistic molecular nucleation studies like density functional methods, not only computer simulations. Classical simulation methods typically use pair potentials, for example combinations of a Lennard-Jones potential and electrostatic Coulomb interaction, to describe the interaction between atoms or molecules. Simple Lennard-Jones potentials represent noble or relatively inert gases quite well. Many-body contributions can also be included by modifying the pair potential according to the location of other atoms or molecules in the environment, or introducing explicit many-body terms which depend on the location of several molecules. A typical example is a polarisable water model, where the point charges located at the two hydrogen and one oxygen site of the model depend on the electric field due to all the other water molecules in the system (Guillot and Guissani 2001). Classical molecular models are often stiff, but the atoms of a molecule can also be attached to each other with springs, and various torsion terms can be used to describe the energy associated with intermolecular interactions. Each classical potential is tuned to reproduce a certain set of measurable properties like liquid density or pair correlation function accurately, but can fail drastically to describe some other properties like saturation vapour pressure or surface tension. This is the case with, for example, water which has proved to be very difficult to model with a classical potential (Guillot 2002). The partial or full proton transfer reactions occurring in pure water, but more importantly in mixtures like water-sulphuric acid, are hard to capture without quantum mechanics. Somewhat surprisingly, rigid non-polarisable water models often predict experimental findings as well, or even better, than flexible potentials with charge transfer.

Ab initio methods (Kohn 1999) are based on the solution of the Schrödinger equation, and, in contrast to classical models, they take the quantum mechanical effects truly into account. *Ab initio*, Latin for "from the beginning", is a slightly misleading term, since there are a number of approximations commonly used within these electron structure calculations:

- For a given system's electron density, electron A has a lower probability density near to electron B due to Coulomb repulsion ("correlation") and Pauli exclusion ("exchange"). The Hartree-Fock method treats exchange exactly, but neglects correlation, and in quantum mechanical density functional methods[1] both exchange and correlation are described approximately.
- Often, only valence electrons are treated explicitly and core electrons are described using fitted pseudopotentials assuming that their state is not affected when the atom forms bonds with other atoms.
- The electronic wave functions can be expressed as a combination of basis set functions, and the choice of these functions may affect the results.

The parameters of classical potentials have often been selected so that they reproduce the cluster structures and energies obtained using *ab initio* simulations. The increasing computer power is also starting to make it possible to use the quantum mechanical approach at non-zero temperatures for clusters relevant to nucleation, as recently demonstrated for water (Dunn et al. 2004).

8.5.2 Extent of system studied

Molecular simulations relevant to gas-liquid nucleation can be classified according to the extent of the system studied. The simulation can mimic the whole supersaturated vapour where clusters are forming and decaying, and we can follow the birth and growth of the cluster that eventually becomes stable and eats up the vapour until a saturation with respect to the droplet surface is reached. We can also study the properties of a single cluster, which is computationally much more efficient, and use the cluster properties to identify the critical size and predict the nucleation rate. The most commonly used cluster

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[1] Not to be confused with the classical density functional theory discussed in section 8.3. In *ab initio* methods the density of electrons is the underlying function, whereas classical density functional theory is based on density of molecules or atoms

property is the formation free energy, but also both truly dynamic growth and decay rates and statistical growth and decay probabilities can be extracted from the simulations.

The definition of a cluster and its lifetime is one major issue in the computer simulations (Reiss et al. 1990; Senger et al. 1999a; Oh and Sorensen 1997; Schaaf et al. 1999). If we know the total (potential + kinetic) energy for all the simulated particles, bound particles can be distinguished from free ones. It must be kept in mind that there are also bound states with positive energy due to the effective potential created by angular momentum. In dynamic studies it has been observed that atoms can travel quite far from the cluster, and still return to it, and thus following the trajectory of a particle even after its energy has turned positive is essential (Harris and Ford 2003; Barrett 2002). In statistical simulations where particle velocity is not explicitly followed, energetic cluster definitions can not be applied, and various geometrical cluster definitions have been developed. The Stillinger (Stillinger 1963) definition treats the cluster as connected networks of molecules: a molecule is part of the cluster if it is closer than some chosen limiting distance from any molecule in the cluster. In the Lee-Barker-Abraham (Lee et al. 1973) definition, molecules inside a sphere centered at the centre of mass of the cluster are part of the cluster, and the choice of the radius of this sphere is ambiguous, just like the choice of Stillinger's distance.

8.5.3 Simulation methods

The simulation methods can roughly be divided into three categories: molecular dynamics (MD), Monte Carlo (MC), and search for the minimum energy configurations. Molecular dynamics (Binder et al. 2004) is a numerical solution of Newton's equations, it describes the dynamic behaviour of the system, and we can follow the trajectory of atoms or molecules and answer questions like how long does cluster formation take. Although dynamic Monte Carlo methods also exist (Gentile 2001) the variations of the Monte Carlo method (Metropolis and Ulam 1949; Metropolis et al. 1953; Yao et al. 1982) used in nucleation studies are based on calculating statistical averages of cluster properties in different ensembles depending on which control parameters (temperature, pressure, total energy, volume, chemical potential) are kept constant in the studied system. In principle, MD is the only realistic way to simulate nucleating clusters, since statistical averages are related to equilibrium systems, and nucleation is essentially a non-equilibrium process.

Monte Carlo methods are computationally much faster than MD, and many nucleation studies have been performed with MC. Simultaneous temperature control of clusters and vapour around it has also proved to be problematic in molecular dynamics, but using Monte Carlo methods constant temperature simulations are straightforward.

Especially when using *ab initio* methods, simulations are often used only to calculate the most stable configuration of a cluster at absolute zero temperature (Ianni and Bandy 1999; Larson et al. 1999; Maheshwary et al. 2001; Bandy and Ianni 1998; Re et al. 1999). The moments of inertia and force constants for this configuration (and possibly and a set of slightly modified arrangements) are used to estimate the rotational and vibrational contributions to the enthalpy H and entropy S. With enthalpy and entropy values known, the free energy at non-zero temperatures is then calculated using the textbook formula $G = H - TS$.

8.5.4 Examples of nucleation studies with molecular methods

The vast majority of computer simulations have been performed using Lennard -Jones potentials, which represent some noble gases like argon rather well. The choice is not so much due to practical interest in the nucleation of this kind of gas, but due to the computational simplicity of the Lennard-Jones (LJ) potential. New theoretical methods and computational algorithms are often first tested with a LJ fluid, because the simulations are fast and many features of the fluid and LJ clusters have already been studied, providing good opportunities for checking and comparison. Most MC studies have aimed at determination of free energy and identification of the critical cluster (Chen et al. 2001; Hale and Ward 1982; Kusaka 2003; Kusaka and Oxtoby 1999; Oh and Zeng 1999, 2000; Senger et al. 1999b), and some MD studies also belong to this category (McGinty 1973; Laasonen et al. 2000). Toxvaerd and Zhukhovitski performed direct molecular dynamic nucleation simulations for a LJ fluid (Toxvaerd 2001, 2002; Zhukhovitskii 1995). Napari and Vehkamäki (2004) studied lifetimes of LJ clusters. Researchers have also studied MD growth and decay rates (Ford and Harris 2004; Napari and Vehkamäki 2004; Schaaf et al. 2001), and MC growth and decay probabilities (ter Horst 2003; Vehkamäki and Ford 2000). Many groups have studied the surface tension of LJ clusters both using MD, MC and density functional theory (Hale 1996; ten Wolde and Frenkel 1998; Moody and Attard 2003; Napari and Laaksonen 2001; Thompson et al. 1984). People have investigated the effect of an inert carrier gas surrounding the nucleating LJ vapour and thus acting as the heat bath which ensures that the temperature stays constant despite ongoing evaporation and condensation (Novikov 1997; Toxvaerd 2003; Yasuoka and Matsumoto 1998a).

The second most studied substance in molecular nucleation is water. Kathmann, Schenter and co-workers (Kathmann et al. 1999; Schenter et al. 1999; Kathmann et al. 2002; Schenter et al. 2002) have studied condensation probabilities, evaporation probabilities and Helmholtz free energies of small water clusters using a Monte Carlo method, and they also report sensitivity of the result to the interaction potential model at temperature 243K. They have used both non-polarisable and polarisable rigid water models. Kusaka and co-workers (Kusaka et al. 1998; Kusaka and Oxtoby 2000) have proposed a method for identifying physical clusters and their equilibrium size distribution, and have applied it for rigid, non-polarisable water (298K) and polarisable water-hydronium ion clusters (200K and 300K). Gao et al.(1999) have studied the effect of an external electric field on the vapour-liquid coexistence curve and formation free energies (the latter at 298K and 323K) of a cluster made of rigid, non-polarisable water molecules. Hale and DiMattio (2000) and Merikanto et al. (2004) have shown that a rigid, non-polarisable water model reproduces the experimental temperature and saturation ratio dependence of the nucleation rate, although the absolute values of the rates are off by a constant factor. The need of a constant correction factor can be attributed to ambiguities regarding the pre-exponential factor in classical nucleation theory, or a constant level shift of the formation energies. Yasuoka and Matsumoto (1998) have studied nucleation of water in the presence of a thermostatted (350K) carrier gas directly by molecular dynamics. They obtained nucleation rates orders of magnitude lower and critical clusters far larger than the classical nucleation theory predictions and experimental results.

Simulation groups have also studied nucleation barriers of n-alkanes (Chen and Tsai 2002), polar model fluid described using Stockmayer potential (ten Wolde et al. 1999; Oh et al. 1998), and Ising model (Vehkamäki and Ford 1999; Wonczak et al. 2000).

Summary

At present, molecular nucleation models can only be applied to hypothetical test systems. Predicting nucleation rates for real experimental substances is either impossible due to lack of realistic interaction models between real molecules, or enormous computational costs. Even if an interaction potential modelling a real substance like water is used in simulations, the results apply only to the model water rather than to real water. The great advantage of classical nucleation theory is that only basic thermodynamic data (density, surface tension, saturation vapour pressures and activities) are needed to apply the theory. For complex mixtures even these data are not often available, or there are incompatible experimental results in the literature. The nucleation rates predicted by classical theory can be several orders of magnitude off the experimental results. However, the dependencies on temperature and saturation ratio are rather correct (as seen in section 5.5), and it must be kept in mind that the nucleation rate is an exponential function of the key quantity, formation free energy, and it is extremely sensitive to small inaccuracies in the thermodynamic description. Improvements to classical theory are disputable and often they do not lead to better agreement with experiments.

When searching for possible nucleation agents classical thermodynamics is very useful: we should look for compounds that have very low saturation vapour pressure, and preferably also low surface tension. Especially promising are substances with vanishingly small saturation vapour pressures over some solution; sulphuric acid has a very strong tendency to nucleate with water, which can be already seen from the fact that the activity coefficient of sulphuric acid in water solution is small.

For most practical purposes, classical nucleation theory is still the only means of predicting nucleation rates and critical cluster sizes. More accurate thermodynamic data can be obtained by measurements if the nucleation process in question is considered important. In practice we are often interested in the value of vapour concentration required for significant nucleation (see activity plots in section 6.2), rather than the actual nucleation rate, and when the results of classical theory are looked upon from this angle, they agree well with the experiments.

Classical nucleation theory is a neat example of how thermodynamics and kinetic theory can be put together to form a complete description of a measurable physical process – a process which remains extremely topical. Nucleated clusters are on the verge of the microscopic and macroscopic world: they are typically too large to be treated on a molecular level, but too small to be safely within the scope of continuum theories like thermodynamics. In the cases where critical clusters are large, thermodynamic description of nucleation is well grounded, but when critical clusters consist of only a few molecules, the justification of the thermodynamic description is doubtful. It is, however, surprising how small clusters can be treated with thermodynamics with results in line with experiments. The perfect nucleation theory would be a combination of molecular model and thermodynamics, where the large clusters are treated using thermodynamics, and the really small ones with molecular theory or thermodynamics where key parameters like surface tension and density are size dependent and fitted to data obtained by molecular models.

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