3

Formation free energy

So far we have studied isolated systems : U, V, N_i are constant. Equilibrium is determined by maximum of entropy $\mathcal{S} = \mathcal{S}_{\max}$. 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.
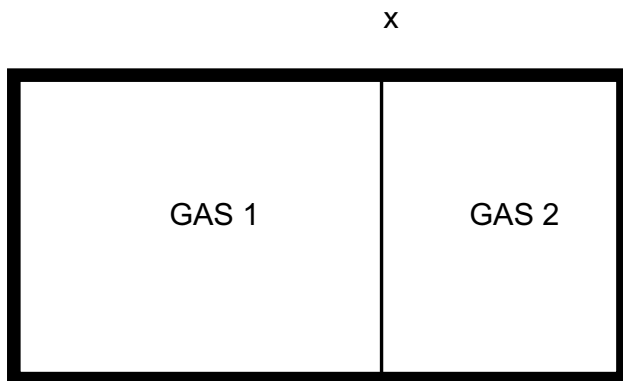

Fig. 3.1. Isolated system with a dividing wall at position x separating two types of gases.

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.
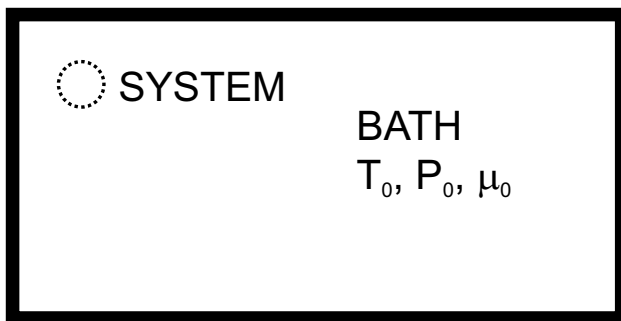

Fig. 3.2. The combination of the system and the bath is isolated. The system is much smaller than the bath.

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:
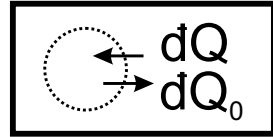
$$đQ_0 = T_0 d\mathcal{S}_0,$$

$$đW_0 = P_0 dV_0.$$

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

$$d\mathcal{S}_{\text{tot}} = d\mathcal{S} + d\mathcal{S}_0 = d\mathcal{S} + \frac{đQ_0}{T_0} = d\mathcal{S} - \frac{đQ}{T_0}. \tag{3.1}$$

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

- Heat balance: heat that entered the system $đQ$ left the bath. Heat that entered the bath is then $đQ_0 = -đQ$

- Work done by the system $đW$ enters the bath.
  Work done by the bath is $đW_0 = -đW$
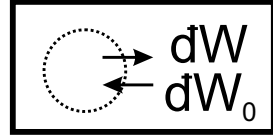
- Total volume is conserved:
  Volume change of the system dV.
  Volume change of the bath is $dV_0 = -dV$

- Particles that entered the system left the bath $dN_i = -dN_{i,0}$ but also the energy they carried must balance: $\mu_i dN_i = -\mu_{i,0} dN_{i,0}$
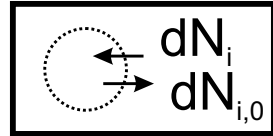
First law for the system reads

$$dU = đQ - đW + \sum_i \mu_i dN_i.$$

We solve the heat $đQ$ entering the system from the first law

$$đQ = dU + đW - \sum \mu_i dN_i$$

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

$$đQ = dU - đW_0 + \sum \mu_{i,0} dN_{i,0}.$$

Then we use reversible forms for the changes in bath properties

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

and the conservation laws again to return to the system properties

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

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

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

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*

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

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:
  $\varphi_{\text{eq}} = F_{\text{eq}} = U - T_0\mathcal{S}$, $dF_{\text{eq}} = dU - T_0 d\mathcal{S} - \mathcal{S} dT_0$
  For reversible changes
  $dU = Td\mathcal{S} - PdV + \sum \mu_i dN_i$ and
  $dF_{\text{eq}} = Td\mathcal{S} - PdV + \sum \mu_i dN_i - T_0 d\mathcal{S} - \mathcal{S} dT_0$
  In equilibrium, the temperature is the same as in the bath, $T = T_0$, which leads to
  $dF_{\text{eq}} = -\mathcal{S} dT_0 - PdV + \sum \mu_i dN_i$,
  which shows that

  $$\mu_i = \left(\frac{\partial F_{\text{eq}}}{\partial N_i} \right)_{T,V,N_{i \neq j}}. \tag{3.3}$$

  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:
  $\varphi_{\text{eq}} = G_{\text{eq}} = U - T_0\mathcal{S} + P_0 V$, and for reversible changes
  $dG_{\text{eq}} = dU - T_0 d\mathcal{S} - \mathcal{S} dT_0 + P_0 dV + V dP_0$
  In equilibrium, the pressure and temperature are set by the bath, $P = P_0$ and $T = T_0$, which results in
  $\Rightarrow dG_{\text{eq}} = -\mathcal{S} dT_0 + V dP_0 + \sum \mu_i dN_i$,

  $$\mu_i = \left(\frac{\partial G_{\text{eq}}}{\partial N_i} \right)_{T,P,N_{i \neq j}}. \tag{3.4}$$

  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
  $\varphi_{eq} = H_{eq} = U + P_0 V$
   For reversible changes in equilibrium where $P = P_0$
  $dH_{eq} = -V dP_0 + T d\mathcal{S} + \sum \mu_i dN_i$
  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, $C_p = (\partial H/\partial T)_P = (\dđ Q/\partial T)_P$.
- For a system connected with particle and temperature bath with $\mu_{i,0}, T_0$
  $\varphi_{eq} = \Omega_{eq} = U - T_0 \mathcal{S} - \sum \mu_{i,0} dN_i$
  For reversible changes in equilibrium $T = T_0, \mu_i = \mu_{i,0}$
  $d\Omega_{eq} = -\mathcal{S} dT_0 - P dV - \sum N_i d\mu_{i,0}$
  Grand potential Ω is a good thermodynamic potential for systems which interact with the environment by exchanging heat and particles.

These show nicely that

$$
\begin{array}{ll}
\text{for constant } T_0, V, N_i & F_{eq} \text{ is constant} \\
\text{for constant } T_0, P_0, N_i & G_{eq} \text{ is constant} \\
\text{for constant } P_0, \mathcal{S}, N_i & H_{eq} \text{ is constant} \\
\text{for constant } T_0, V, \mu_{i,0} & \Omega_{eq} \text{ is constant}
\end{array}
$$

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 $dG_{eq} = -\mathcal{S} dT_0 + V dP_0 + \sum \mu_i dN_i$. We can immediately see that the partial derivatives of the free energy give thermodynamic variables

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

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

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

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.

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

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

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

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

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

Grand potential Ω

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

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

Gibbs free energy G (also here for completeness)

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

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

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.
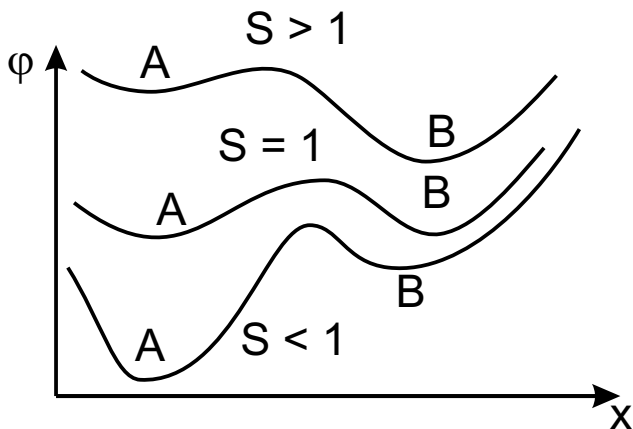

Fig. 3.3. Free energy curves as functions of density x with different saturation ratios S.

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 $S = \dfrac{P}{P_e(T)}$ 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
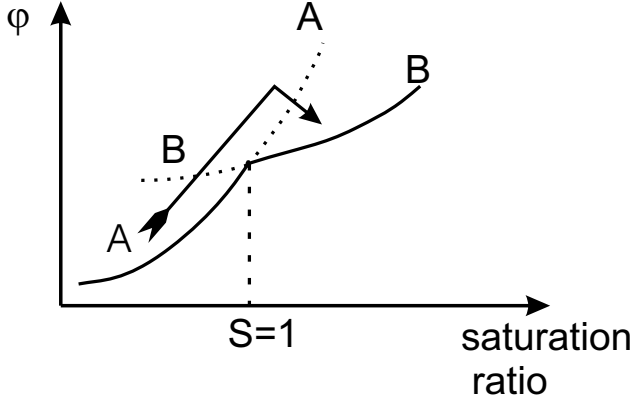
Fig. 3.4. Free energy in the equilibrium system as a function of saturation ratio S. The points forming the curves correspond to the location of the minima A and B in Fig. 3.3. The arrow shows the route taken by a vapour when saturation is exceeded, it follows the metastable part of curve A until disturbance, 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

$$U_0 = T_0 \mathcal{S}_0 - P_0 V_0 + \sum \mu_{i,g}^0 N_{i,g}^0.$$

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

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

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

$$\Omega_0 = U_0 - T_0 \mathcal{S}_0 - \sum \mu_{i,g}^0 N_{i,g}^0 = -P_0 V_0 = -P_0(V_l + V_g)$$

and in the final state

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

The grand free energy change in the droplet formation is then

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

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

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

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 $N_{i,\text{tot}} = N_{i,l} + N_{i,g} + N_{i,s} = N_{i,g}^0$.
   Then the Gibbs free energies in the initial and final states are

$$G_0 = U_0 - T_0 \mathcal{S}_0 + P_0 V_0 = \sum \mu_{i,g}^0 N_{i,g}^0 \qquad (3.7)$$
$$G = U - T_0 \mathcal{S} + P_0 V_{\text{tot}} = U - T_0 \mathcal{S} + P_0(V_g + V_l) \qquad (3.8)$$
$$= (P_0 - P_l)V_l + \sigma A + \sum \mu_{i,g} N_{i,g} + \sum \mu_{i,l} N_{i,l} + \sum \mu_{i,s} N_{i,s}.$$

The Gibbs free energy change in the droplet formation is

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

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

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

we get

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

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

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

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

$$F_0 = U_0 - T_0 \mathcal{S}_0 = -P_0(V_l + V_g) + \sum \mu_{i,g}^0 N_{i,g}^0$$

$$F = U - T_0 \mathcal{S} = -P_g V_g - P_l V_l + \sigma A$$

$$+ \sum \mu_{i,l} N_{i,l} + \sum \mu_{i,g} N_{i,g} + \sum \mu_{i,s} N_{i,s}.$$

The change in the Helmholtz free energy is

$$\Delta F = (P_0 - P_l)V_l + (P_0 - P_g)V_g + \sigma A$$

$$+ \sum (\mu_{i,g} - \mu_{i,g}^0) N_{i,g} + \sum (\mu_{i,l} - \mu_{i,g}^0) N_{i,l} + \sum (\mu_{i,s} - \mu_{i,g}^0) N_{i,s}.$$

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:

$$\Omega \neq \Omega_l + \Omega_g + \Omega_s$$
$$G \neq G_l + G_g + G_s$$
$$F \neq F_l + F_g + F_s$$

$\Omega_l, \Omega_g, \Omega_s$ 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 $\Delta\Omega, \Delta F$ 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.*

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

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.
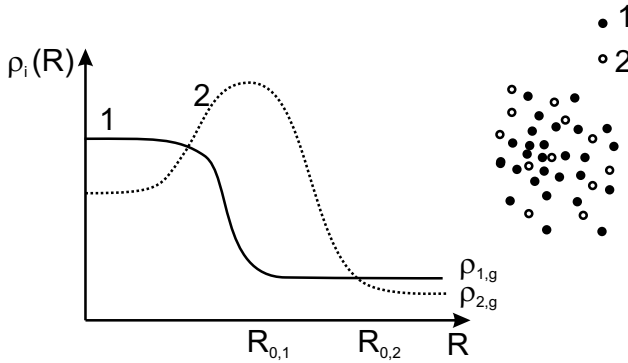

Fig. 3.5. Molecular densities of components 1 and 2 as functions of distance from the centre of a real spherical droplet and a picture of the molecular positions in the droplet (cluster). $\rho_{1,g}$ and $\rho_{2,g}$ are the densities of the two components in the vapour far from the droplet. $R_{0,i}$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

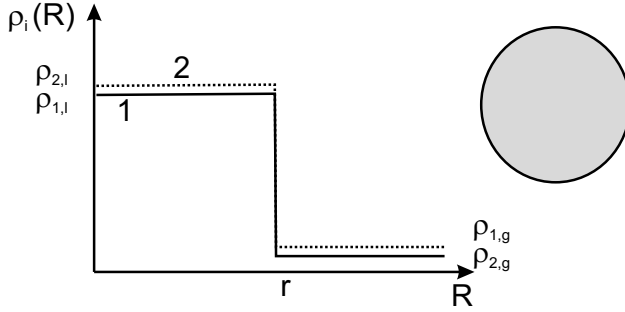$$\frac{\Delta\mu_i}{v_{i,l}} = \frac{\Delta\mu_1}{v_{1,l}} \tag{3.10}$$

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

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

$$= T_0 \mathcal{S}_{\text{tot}}^* - P_l^* V_l^* - P_g^0 V_g^* + \sigma^* A^* + \sum \mu_{i,g}^0 N_{i,\text{tot}}. \qquad (3.11)$$

If we now move the dividing surface, but keep the physical situation unchanged U^*, T_0, $\mathcal{S}_{\text{tot}}^*$, $\mu_{i,g}^0$, $N_{i,\text{tot}}^*$, 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*

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

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)

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

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)

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

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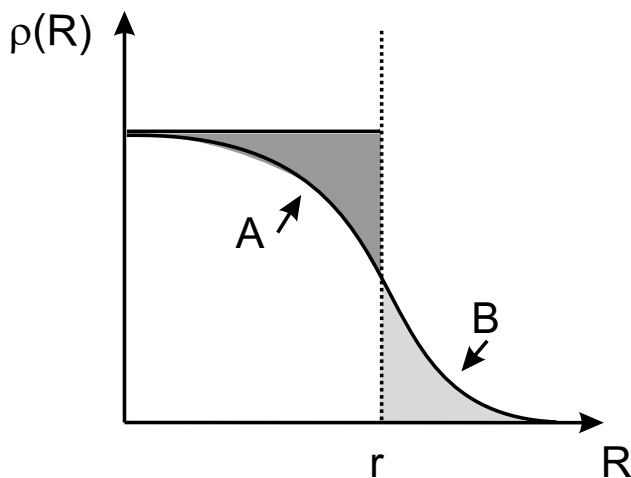
Fig. 3.7. Density as a function of the distance from the centre of a spherical cluster in one-component system. The dashed line illustrates the position of the equimolar surface for which areas A and B are equal.
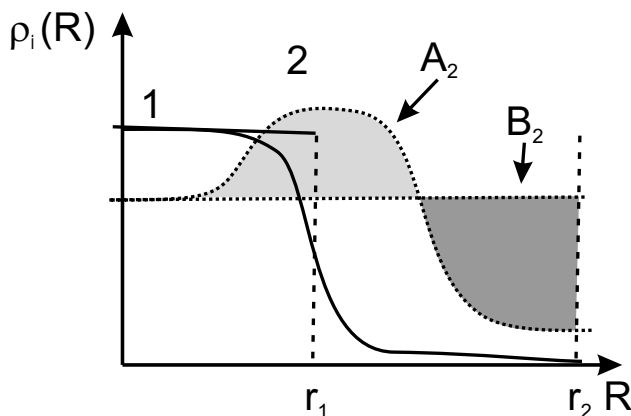

Fig. 3.8. Densities of components 1 and 2 as a function of the distance from the centre of a spherical cluster in a two-component system. Radius r_2 illustrates the position of the equimolar surface for component 2 for which areas A_2 and B_2 are equal, and r_1 is the equimolar surface for component 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)

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

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

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

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

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

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

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

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

$$\Delta\varphi = \Delta\mu N_d + \sigma A = -N_d kT_0 \ln S + \sigma A.$$

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

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

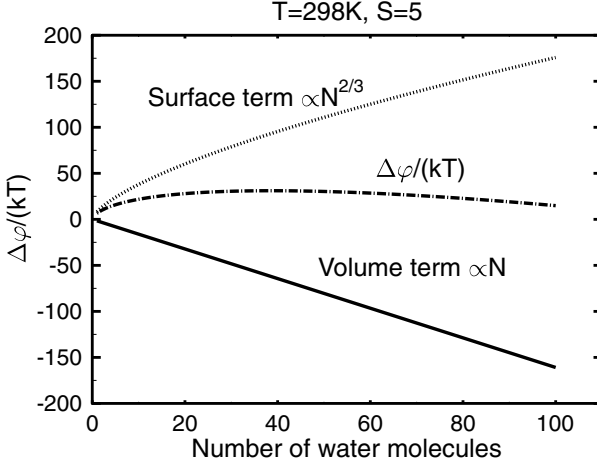Inserting this to the expression of the formation free energy gives

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.
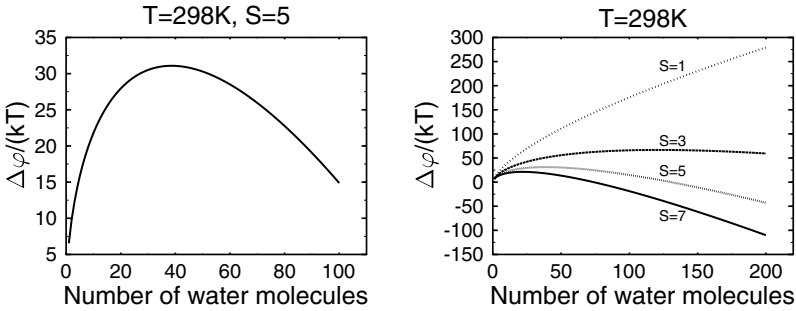

Fig. 3.10. Droplet formation free energy as a function of the number of molecules in the droplet for pure water with different saturation ratios S.

$$\Delta\varphi = -N_d kT_0 \ln S + N_d^{2/3} \sigma (36\pi)^{1/3} v_l^{2/3}, \qquad (3.16)$$

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 $\left(\dfrac{\partial^2 S}{\partial x^2}\right) = 0$, 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*.
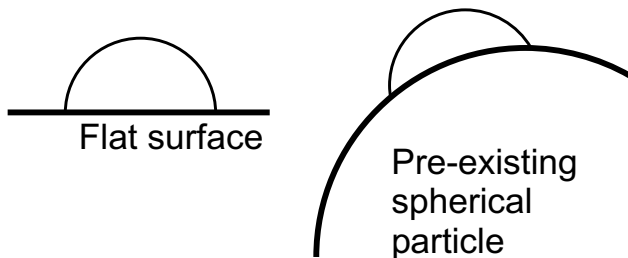

Fig. 3.11. Droplet formation on a pre-existing flat surface and spherical particle.

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.
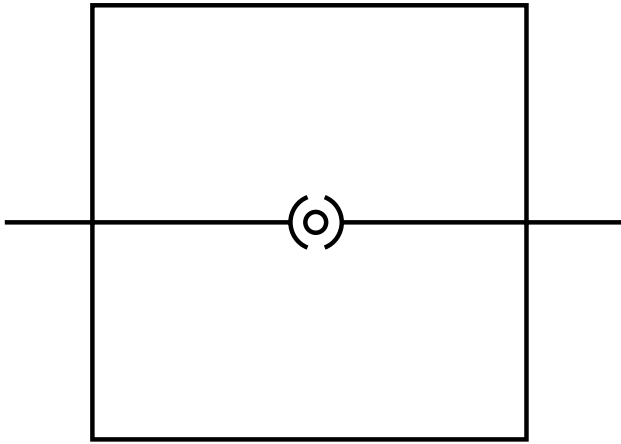

Fig. 3.12. Imaginary tweezers holding a non-equilibrium cluster together.

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) $d\mu = v dP$ in the gas (for ideal gas $PV = NkT_0$ and $v_g = \dfrac{kT_0}{P}$) 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 $S' = \dfrac{P_g'}{P_e(T_0)}$. 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

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

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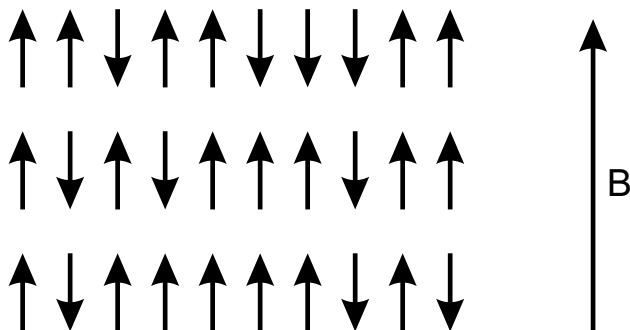
Fig. 3.13. Schematic figure of array of spins in a magnetic field $\mathcal{B}$.
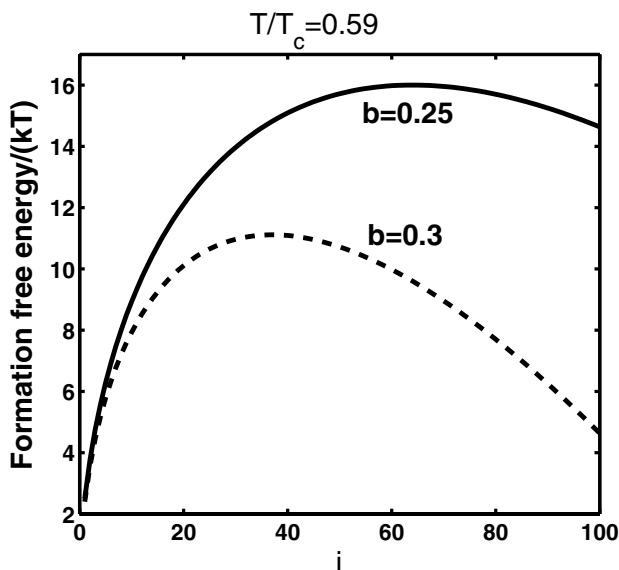

Fig. 3.14. Formation free energy as a function of the cluster size for two magnetic field values in a three dimensional Ising model. For temperature $T/T_c = 0.59$ surface tension parameter has the value $\zeta = 3$ (Heermann et al. 1984).

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)

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

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 $(\mu_{i,s} - \mu_{i,g}^0)$, which fortunately disappeared from the free energy formula in the one-component system.

For non-critical clusters $\mu_{i,s} \neq \mu_{i,g}^0$, 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 $(\mu_{i,s} - \mu_{i,g}^0)$ as

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

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

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

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

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)

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

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

$$\left(\frac{\partial \mu_{i,s}}{\partial x_{j,l}}\right)_{x_{k \neq j,l,r}} = \left(\frac{\partial \mu_{i,l}}{\partial x_{j,l}}\right)_{x_{k \neq j,l,r}}$$

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

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)

$$N_{2,s} = \frac{A\dfrac{d\sigma}{dx_{2,l}}}{\dfrac{v_{2,l}}{v_{1,l}}\left(\dfrac{\partial \mu_{1,l}}{\partial x_{2,l}}\right) - \left(\dfrac{\partial \mu_{2,l}}{\partial x_{2,l}}\right)}$$

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

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

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

$$= \sum \Delta\mu_i N_{i,l} + \sigma A + \sum \left(\Delta\mu_i + \frac{2\sigma v_{i,l}}{R}\right) N_{i,s}$$

$$= \sum \Delta\mu_i (N_{i,l} + N_{i,s}) + \sigma A + \frac{2\sigma}{R} \sum v_{i,l} N_{i,s}$$

$$\Delta\varphi = \sum_i \Delta\mu_i N_{i,d} + \sigma A, \qquad (3.29)$$

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

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

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

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

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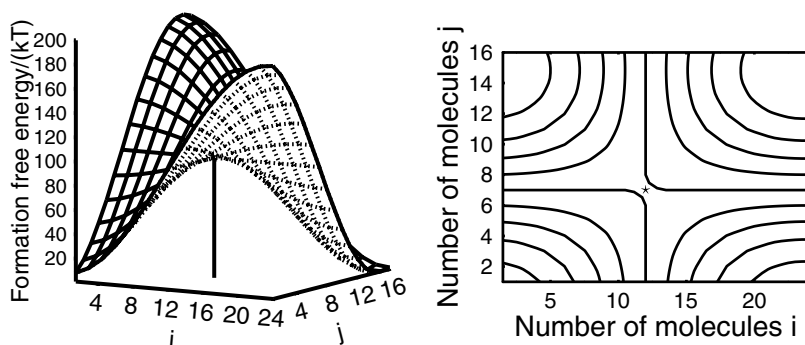

Fig. 3.15. Formation free energy as a function of the numbers of molecules of two components. The left-hand figure shows the three-dimensional surface and the right-hand figure is a contour plot of the same surface. Critical size is marked with a vertical line in the surface plot and a star in in contour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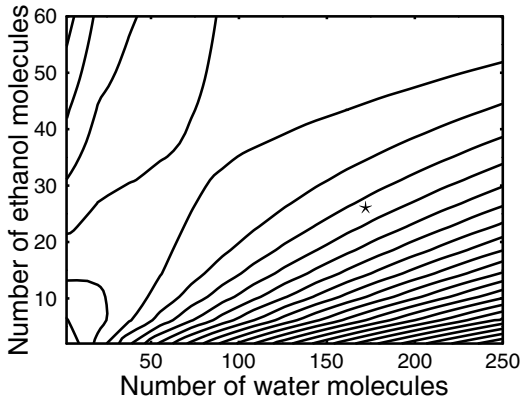

Fig. 3.16. The free energy surface for water-ethanol mixture with the surface excess molecules neglected. Temperature is $T=260$K, gas phase activities of the two components are equal $\mathcal{A}_{1,g} = \mathcal{A}_{2,g} = 1.5$. The critical size (172 water molecules, 26 ethanol molecules) given by 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 $\Delta\mu = -kT\frac{A_{i,g}}{A_{i,l}(x_{i,l})}$ 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

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

- 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/m³.

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/m³.
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
$\Delta\mu_1 + \frac{2\sigma v_{1,l}}{r} - 4\pi r^2 \left(\frac{\partial\sigma}{\partial x}\right) x \frac{1}{N_{1,l}+N_{2,l}} = 0$ and
$\Delta\mu_2 + \frac{2\sigma v_{2,l}}{r} + 4\pi r^2 \left(\frac{\partial\sigma}{\partial x}\right) (1-x)\frac{1}{N_{1,l}+N_{2,l}} = 0$,
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):
$P_{w,e}^o = \exp[77.34 - 7235.42/T - 8.2\ln(T) + 0.00571T]$ and
$P_{e,e}^o = 6.137 \cdot 10^6$
$\cdot \exp\{[-8.4565739(1 - T/513.92) + 0.090430576(1 - T/513.92)^{1.5}$
$-4.83483(1 - T/513.92)^3 + 3.7610779(1 - T/513.92)^6]513.92/T\}$.
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.