

Statistical Mechanics

University of Cambridge Part II Natural Sciences Tripos

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1 Fundamentals of Statistical Mechanics

1.1 Principle of Equal *A Priori* Probabilities

Postulate 1.1 (Principle of equal *a priori* probabilities). A system with fixed N , V and E is likely to be found in any of its $\Omega(E)$ energy eigenstates.

Remark. This is one of the fundamental assumptions of statistical mechanics, and it is non-provable. Some justifications of this assumption includes Boltzmann's H-theorem and Liouville theorem.

Consider a system with total energy E that consists of two weakly interacting subsystems, which means that they can only exchange energy, as shown in figure 1.1. The energy is distributed over the two subsystems such that

$$E_1 + E_2 = E. \quad (1.1)$$

For a given E_1 , the total number of degenerate states of the system is $\Omega_1(E_1) \times \Omega_2(E_2)$. We choose take the logarithm of degeneracy so that the value is extensive. This gives

$$\ln \Omega(E_1, E - E_1) = \ln \Omega_1(E_1) + \ln \Omega_2(E_2). \quad (1.2)$$

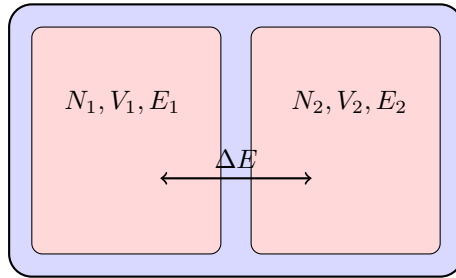


Figure 1.1: Two weakly coupled systems that can exchange energy such that the total energy of the universe is conserved to be E .

By the principle of equal *a priori*, the most likely value of E_1 is the one that maximises $\ln \Omega(E_1, E - E_1)$, i.e.

$$\left(\frac{\partial \ln \Omega(E_1, E - E_1)}{\partial E_1} \right)_{N, V, E} = 0. \quad (1.3)$$

Using the fact that $dE_1 = dE_2$, we obtain the condition

$$\left(\frac{\partial \ln \Omega_1(E_1)}{\partial E_1} \right)_{N_1, V_1} = \left(\frac{\partial \ln \Omega_2(E_2)}{\partial E_2} \right)_{N_2, V_2}. \quad (1.4)$$

We define

$$\beta(E, V, N) := \left(\frac{\partial \ln \Omega(E, V, N)}{\partial E} \right)_{N, V}, \quad (1.5)$$

the the equilibrium condition becomes

$$\beta(E_1, V_1, N_1) = \beta(E_2, V_2, N_2). \quad (1.6)$$

1.2 Boltzmann Entropy

The thermal equilibrium condition of equal β must be equivalent to the condition that the two subsystems having the same temperature (from classical Thermodynamics). Also, just like the thermodynamic entropy S , $\ln \Omega$ is a state function of E , V and N . Moreover, when the thermal equilibrium is reached, $\ln \Omega$ of the total system is maximised, just as S . This suggests that $\ln \Omega$ is a monotonically increasing function of entropy S . Since both S and $\ln \Omega$ are extensive, S is proportional to $\ln \Omega$

$$S(N, V, E) = k_B \ln \Omega(N, V, E) \quad (1.7)$$

for some constant k_B known as the *Boltzmann's constant*.

Remark. In the statistical picture, the second law of thermodynamics states that, at thermal equilibrium, the system is most likely to be found in the state that has the largest number of degenerate energy states.

1.3 Temperature

The thermodynamic definition of temperature is

$$\frac{1}{T} := \left(\frac{\partial S}{\partial E} \right)_{V, N}, \quad (1.8)$$

which is obtained from the fundamental equation for the internal energy

$$dE = TdS - PdV + \mu dN. \quad (1.9)$$

Hence β and temperature T is related by

$$\beta = \frac{1}{k_B T}. \quad (1.10)$$

1.4 The Third Law

The third law of thermodynamics states that at $T = 0$, the number of accessible states of a pure substance is equal to one (i.e. $\Omega = 1$, so that $\ln \Omega = 0$). In other words: at absolute zero, the system is in its ground state – and this ground state is non-degenerate.

1.5 System at Constant Temperature

Now let's consider a system that is at thermal equilibrium with a large heat bath. The total system is isolated so that $E_{\text{tot}} = E_{\text{bath}} + E_{\text{sys}}$ is fixed. The system is weakly coupled to the bath so they can exchange energy. Suppose the system is prepared in a specific state $|i\rangle$ with energy E_i , then the bath has an energy $E_{\text{bath}} = E_{\text{tot}} - E_i$ with degeneracy $\Omega_{\text{bath}}(E_{\text{tot}} - E_i)$. The degeneracy of the whole system is $\Omega = \Omega_{\text{sys}} \Omega_{\text{bath}} =$

Ω_{bath} . The principle of equal *a priori* applies only to an isolated system, so all the state of the universe with total energy E_{tot} are equally likely to occur. Hence, the probability of finding the system in state $|i\rangle$ is given by

$$P_i = \frac{\Omega_{\text{bath}}(E_{\text{tot}} - E_i)}{\sum_{|j\rangle} \Omega_{\text{bath}}(E_{\text{tot}} - E_j)}. \quad (1.11)$$

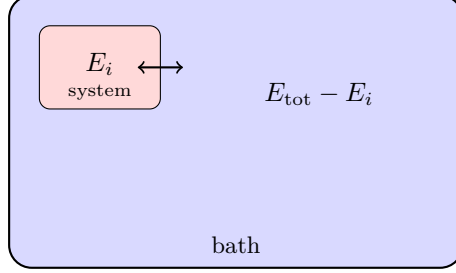


Figure 1.2: The system can exchange energy with the surrounding bath, such that the overall universe has fixed total energy E_{tot} .

Since the bath is very much larger than the system of interest, most of the energy of the universe will be in the bath. To compute $\Omega_{\text{bath}}(E_{\text{tot}} - E_i)$, we expand $\ln \Omega_{\text{bath}}(E_{\text{tot}} - E_i)$ about $E_{\text{bath}} = E_{\text{tot}}$

$$\ln \Omega_{\text{bath}}(E_{\text{tot}} - E_i) = \ln \Omega_{\text{bath}}(E_{\text{tot}}) - E_i \left(\frac{\partial \ln \Omega_{\text{bath}}(E)}{\partial E} \right)_{E=E_{\text{tot}}} + \mathcal{O}\left(\frac{1}{E}\right), \quad (1.12)$$

or,

$$\ln \Omega_{\text{bath}}(E_{\text{tot}} - E_i) = \ln \Omega_{\text{bath}}(E_{\text{tot}}) - \beta E_i + \mathcal{O}\left(\frac{1}{E}\right). \quad (1.13)$$

Hence,

$$P_i = \frac{\exp(-\beta E_i)}{\sum_{|j\rangle} \exp(-\beta E_j)} = \frac{\exp(-\beta E_i)}{Q}. \quad (1.14)$$

This is the *canonical distribution*, or *Boltzmann Distribution*. It describes the probability of the whole system being found in a particular microstate. The Boltzmann distribution should not be confused with the Maxwell–Boltzmann distribution (the distribution of the particle speeds in ideal gases) or Maxwell–Boltzmann statistics (the distribution of classical particles over energy states in thermal equilibrium).

In equation (1.12), we have ignored higher order terms in the Taylor expansion and claimed that it is $\mathcal{O}(1/E)$. This is straightforward to prove. The next term in the expansion is

$$\frac{E_i^2}{2} \left(\frac{\partial^2 \ln \Omega_{\text{bath}}(E)}{\partial E^2} \right)_{E=E_{\text{tot}}} = \frac{E_i^2}{2} \left(\frac{\partial \beta}{\partial E} \right)_{E=E_{\text{tot}}} = -\frac{E_i^2}{2k_B T^2 C_{V,\text{bath}}}, \quad (1.15)$$

where we have used

$$C_V = \left(\frac{\partial E}{\partial T} \right)_{N,V} = \left(\frac{\partial E}{\partial \beta} \right)_{N,V} \left(\frac{\partial \beta}{\partial T} \right)_{N,V}. \quad (1.16)$$

Since both the heat capacity and the total energy are extensive, we can conclude that this term is $\mathcal{O}(1/E)$ as claimed.

1.5.1 Link to Thermodynamics

Knowing the energy distribution (1.14) allows us to compute the average energy of the system at a given temperature

$$\langle E_{\text{sys}} \rangle = \sum_{|i\rangle} E_i P_i = \frac{\sum_{|i\rangle} \exp(-\beta E_i)}{Q}. \quad (1.17)$$

Next we note that the numerator looks very similar to the definition of Q . If we differentiate Q with respect to β , we obtain the negative of the numerator, and so we can write

$$\langle E_{\text{sys}} \rangle = -\frac{1}{Q} \left(\frac{\partial Q}{\partial \beta} \right)_{N,V} = - \left(\frac{\partial \ln Q}{\partial \beta} \right)_{N,V}. \quad (1.18)$$

We can change the differential variable to T instead

$$\langle E_{\text{sys}} \rangle = - \left(\frac{\partial \ln Q}{\partial T} \right)_{N,V} \frac{\partial T}{\partial \beta} = k_B T^2 \left(\frac{\partial \ln Q}{\partial T} \right)_{N,V}. \quad (1.19)$$

We can compare this to the thermodynamic relation

$$E = -T^2 \left(\frac{\partial (A/T)}{\partial T} \right)_{N,V}, \quad (1.20)$$

which can be easily derived by differentiating A/T , we can see that the Helmholtz free energy A is related to the partition function through the bridge relation

$$A = -k_B T \ln Q. \quad (1.21)$$

1.6 Fluctuations

Again consider a system of N particles with volume V in the large thermal bath. In this case, the probability of finding the system in any of the $\Omega(N, V, E)$ states with energy E is

$$P(E) = \frac{\Omega(N, V, E) \exp(-\beta E)}{\sum_{|i\rangle} \exp(-\beta E_i)}. \quad (1.22)$$

Using the definition of entropy, we may rewrite this at

$$P(E) \sim \exp(-\beta E) \exp\left[\frac{S(N, V, E)}{k_B}\right]. \quad (1.23)$$

The most likely energy of the system, E^* , is the one for which

$$\left. \frac{\partial P(E)}{\partial E} \right|_{E=E^*} = 0 \quad \Rightarrow \quad \left(\frac{\partial S}{\partial E} \right)_{E=E^*} = \frac{1}{T}. \quad (1.24)$$

We can expand S in a Taylor series about E^* and define $\Delta E := E - E^*$, we obtain

$$\frac{S(N, V, E)}{k_B} = \frac{S(N, V, E^*)}{k_B} + \frac{1}{k_B T} \Delta E + \frac{1}{2k_B} \left(\frac{\partial^2 S}{\partial E^2} \right) (\Delta E)^2 + \mathcal{O}((\Delta E)^3). \quad (1.25)$$

Take logarithm of expression (1.23) and use the expansion (1.25), we can see that

$$\ln P(E^* + \Delta E) = c + \frac{1}{2k_B} \left(\frac{\partial^2 S}{\partial E^2} \right) (\Delta E)^2 + \mathcal{O}((\Delta E)^3), \quad (1.26)$$

where c is a constant independent of ΔE . The term linear in ΔE vanishes. In the limit of large N , we can ignore terms of order $(\Delta E)^3$ or above and find that

$$P(E + \Delta E) = c' \exp \left[\frac{1}{2k_B} \left(\frac{\partial^2 S}{\partial E^2} \right) (\Delta E)^2 \right], \quad (1.27)$$

where c' is another constant. We now recall the standard thermodynamics relation

$$\left(\frac{\partial^2 S}{\partial E^2} \right) = \left(\frac{\partial(1/T)}{\partial E} \right)_V = -\frac{1}{T^2} \left(\frac{\partial T}{\partial E} \right)_V = -\frac{1}{T^2} \left(\frac{\partial E}{\partial T} \right)_V^{-1} = -\frac{1}{C_V T^2}. \quad (1.28)$$

Finally, we normalise the probability density to obtain

$$P(E^* + \Delta E) = (2\pi k_B T^2 C_V)^{-1/2} \exp \left[-\frac{(\Delta E)^2}{2k_B T^2 C_V} \right], \quad (1.29)$$

or

$$P(E) = (2\pi k_B T^2 C_V)^{-1/2} \exp \left[-\frac{(E - E^*)^2}{2k_B T^2 C_V} \right]. \quad (1.30)$$

This is a Gaussian distribution. We can see that the mean squared fluctuation in the energy of a system at constant N , V and T is directly related to the heat capacity C_V ,

$$\sigma_E^2 = \langle (\Delta E)^2 \rangle = k_B T^2 C_V. \quad (1.31)$$

In fact, whilst the result that the probability distribution function is a Gaussian is important, it is possible to compute the variance of the distribution in a much simpler way. The thermal average of the energy is

$$\langle E \rangle = \frac{\sum_{|i\rangle} E_i e^{-\beta E_i}}{Q} = -\frac{1}{Q} \frac{\partial Q}{\partial \beta}, \quad (1.32)$$

and hence the derivative of $\langle E \rangle$ with respect to β is

$$\frac{\partial \langle E \rangle}{\partial \beta} = -\frac{\sum_{|i\rangle} E_i^2 e^{-\beta E_i}}{Q} + \frac{\sum_{|i\rangle} E_i e^{-\beta E_i}}{Q} \frac{1}{Q} \frac{\partial Q}{\partial \beta}. \quad (1.33)$$

This can be simplified to

$$\frac{\partial \langle E \rangle}{\partial \beta} = -\langle E^2 \rangle + \langle E \rangle^2 \equiv -\sigma_E^2. \quad (1.34)$$

We can related this to the heat capacity at constant volume

$$C_V = \left(\frac{\partial E}{\partial T} \right)_{N,V} = \left(\frac{\partial E}{\partial \beta} \right)_{N,V} \frac{\partial \beta}{\partial T} = -\frac{1}{k_B T^2} \left(\frac{\partial E}{\partial \beta} \right)_{N,V}. \quad (1.35)$$

Therefore $\sigma_E^2 = k_B T^2 C_V$ as before.

Since both E and C_V are extensive, we can write $\langle E \rangle = N \langle \epsilon \rangle$ and $C_V = N c_V$, where ϵ and c_V are the energy and heat capacity per particle. The relative variance in the energy vanishes in the thermodynamic limit as $N \rightarrow \infty$, since

$$\frac{\langle (\Delta E)^2 \rangle}{E^2} = k_B T^2 \frac{C_V}{\langle E \rangle^2} = \frac{k_B T^2 c_V}{N \langle \epsilon \rangle^2} \sim \frac{1}{N}. \quad (1.36)$$

Similar results apply to other quantities of interest. Fluctuations about the average are negligible in the thermodynamic limit, and the statistical mechanical average of a thermodynamic property will correspond to its measured value.

1.7 Helmholtz Energy and Equilibrium

By the second law of thermodynamics, in an isolated system at equilibrium, the entropy of a system is maximised. Consider a system in contact with a thermal reservoir such that the total energy is conserved. Note that the system plus the thermal bath is isolated, so we may apply the second law of thermodynamics. The total degeneracy is

$$\Omega_{\text{tot}} = \Omega_{\text{sys}}(E_{\text{sys}}) \Omega_{\text{bath}}(E_{\text{tot}} - E_{\text{sys}}). \quad (1.37)$$

We can Taylor expand $\ln \Omega_{\text{bath}}(E_{\text{tot}} - E_{\text{sys}})$ up to linear order in E_{sys} and find that

$$\ln \Omega_{\text{tot}} = \ln \Omega_{\text{sys}}(E_{\text{sys}}) + \ln \Omega_{\text{bath}}(E_{\text{tot}}) - \beta E_{\text{sys}}. \quad (1.38)$$

The equilibrium condition is that the derivative of $\ln \Omega_{\text{tot}}$ with respect to E_{sys} vanishes. Since $\ln \Omega_{\text{sys}}(E_{\text{tot}})$ is independent of E_{sys} , the equilibrium condition is equivalent to minimising $\beta E_{\text{sys}} - \ln \Omega_{\text{sys}}(E_{\text{sys}}) = \beta(E_{\text{sys}} - TS_{\text{sys}})$. The Helmholtz energy A is defined as

$$A := E - TS. \quad (1.39)$$

Therefore, at constant temperature and volume, A is at a minimum at equilibrium.

1.8 Pressure

Now consider a system that can exchange volume with a reservoir such that the total volume of the system plus the bath is fixed. The condition for equilibrium is that the total entropy is maximised, so we need to determine the maximum of

$$\ln \Omega(V_{\text{sys}}, V_{\text{tot}} - V_{\text{sys}}) \ln \Omega_{\text{sys}}(V_{\text{sys}}) + \ln \Omega_{\text{bath}}(V_{\text{tot}} - V_{\text{sys}}) \quad (1.40)$$

with respect to V_{sys} . Using the definition of entropy,

$$\left(\frac{\partial S_{\text{sys}}}{\partial V_{\text{sys}}} \right)_{E, N} + \left(\frac{\partial S_{\text{bath}}}{\partial V_{\text{sys}}} \right)_{E, N} = 0. \quad (1.41)$$

Since $dV_{\text{sys}} = -dV_{\text{bath}}$,

$$\left(\frac{\partial S_{\text{sys}}}{\partial V_{\text{sys}}} \right)_{E, N} = \left(\frac{\partial S_{\text{bath}}}{\partial V_{\text{bath}}} \right)_{E, N}. \quad (1.42)$$

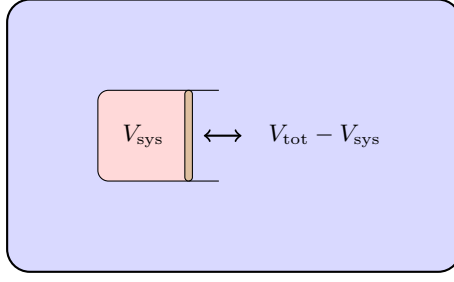


Figure 1.3: A system coupled to the bath such that a piston separating them can change position. The system and the bath can exchange volume.

From thermodynamics, we have

$$dS = \frac{1}{T}dE + \frac{P}{T}dV - \frac{\mu}{T}dN \quad (1.43)$$

and hence $(\partial S/\partial V)_{E,N} = P/T$. Thus the equilibrium condition becomes

$$\frac{P_{\text{sys}}}{T_{\text{sys}}} = \frac{P_{\text{bath}}}{T_{\text{bath}}}. \quad (1.44)$$

If the system can exchange both energy and volume with the bath, then the conditions for equilibrium are $T_{\text{sys}} = T_{\text{bath}}$ and $P_{\text{sys}} = P_{\text{bath}}$.

In practice, it is convenient to use the fundamental relation for the Helmholtz energy, $dA = -PdV - SdT + \mu dN$, and the corresponding expression for the pressure

$$P = - \left(\frac{\partial A}{\partial V} \right)_{T,N} = k_B T \left(\frac{\partial \ln Q}{\partial V} \right)_{T,N}, \quad (1.45)$$

where we have used the bridge relation $A = -k_B T \ln Q$. Later, we shall use the relation to obtain a general expression of the pressure in a system of interacting particles. However, we will need to first derive some further results in classical statistical mechanics.

1.9 Classical Statistical Mechanics

The Thermal average of the expectation value of some observable X is

$$\langle X \rangle = \frac{\sum_{|i\rangle} \exp(-E_i/k_B T) \langle i|X|i\rangle}{\sum_{|i\rangle} \exp(-E_i/k_B T)}. \quad (1.46)$$

This suggests that in order to compute the thermal average, we first need to solve the Schrödinger equation of the many-body system of interest, then we need to compute the expectation value of the operator X for all those quantum states that have non-negligible statistical weight. This approach is doomed for all but the simplest system. Fortunately, this can be simplified to a more workable expression in the classical limit $\hbar \rightarrow 0$. For a d -dimensional, N -particle system, this is given by

$$\langle X \rangle = \frac{\int \prod_{i=1}^N d^d \mathbf{p}_i d^d \mathbf{r}_i \exp(-\beta [\sum_i p_i^2/2m_i + U(\{\mathbf{r}_i\})]) X(\{\mathbf{p}_i, \mathbf{r}_i\})}{\int \prod_{i=1}^N d^d \mathbf{p}_i d^d \mathbf{r}_i \exp(-\beta [\sum_i p_i^2/2m_i + U(\{\mathbf{r}_i\})])}, \quad (1.47)$$

where \mathbf{r}_i and \mathbf{p}_i are the coordinate and momentum of the i^{th} particle. The classical partition function is

$$Q = \frac{1}{h^{dN} N!} \int \prod_{i=1}^N d^3 \mathbf{p}_i d^3 \mathbf{r}_i \exp(-\beta \left[\sum_i^N \frac{p_i^2}{2m_i} + U(\{\mathbf{r}_i\}) \right]), \quad (1.48)$$

where the $1/N!$ factor is to account for the indistinguishability of the particles (the situation is a bit subtle... See *Gibbs' Paradox*.) and $1/h^{dN}$ is to make the partition function dimensionless.

1.9.1 Integration over the Momenta

From now on assume the space is three dimensional. Note that the integration over momenta and spatial coordinates can be separated

$$Q(E, V, T) = \frac{1}{h^{3N} N!} \int \prod_{i=1}^N d\mathbf{p}_i \exp(-\beta \sum_{i=1}^N \frac{p_i^2}{2m}) \int \prod_{i=1}^N d\mathbf{r}_i \exp(-\beta U(\{\mathbf{r}_i\})). \quad (1.49)$$

Let's focus on the first integral. We can resolve p_i into its cartesian components $p_i^2 = p_{ix}^2 + p_{iy}^2 + p_{iz}^2$, as so it can be further factorised

$$\int \prod_{i=1}^N d\mathbf{p}_i \exp(-\beta \sum_{i=1}^N \frac{p_i^2}{2m}) \quad (1.50)$$

$$= \int \prod_{i=1}^N dp_{ix} dp_{iy} dp_{iz} \exp(-\frac{\beta p_{ix}^2}{2m_i}) \exp(-\frac{\beta p_{iy}^2}{2m_i}) \exp(-\frac{\beta p_{iz}^2}{2m_i}). \quad (1.51)$$

These are just $3N$ identical Gaussian integrals, each evaluated as

$$\int_{-\infty}^{\infty} dp \exp(-\frac{\beta p^2}{2m}) = \sqrt{\frac{2m\pi}{\beta}}. \quad (1.52)$$

Hence, the partition function can be written as

$$Q(N, V, T) = \frac{1}{h^{3N} N!} \left(\frac{2m\pi}{\beta} \right)^{3N/2} \int \prod_{i=1}^N d^3 \mathbf{r}_i \exp[-U(\{\mathbf{r}_i\})] \quad (1.53)$$

$$=: \frac{1}{\Lambda^{3N} N!} \int \prod_{i=1}^N d\mathbf{r}_i \exp[-\beta U(\{\mathbf{r}_i\})], \quad (1.54)$$

where $\Lambda := h/\sqrt{2\pi m k_B T}$ is the *de Broglie wavelength*. If the system consists of a mixture of two components A and B , then the classical partition function becomes

$$Q(N_A, N_B, V, T) = \frac{1}{\Lambda^{3(N_A+N_B)} N_A! N_B!} \int \prod_{i=1}^{N_A} \prod_{j=1}^{N_B} d^3 \mathbf{r}_i d^3 \mathbf{r}_j \exp[-\beta U(\{\mathbf{r}_i, \mathbf{r}_j\})]. \quad (1.55)$$

In molecular systems, a purely classical description is inappropriate. In particular, molecular vibrations and sometimes rotations have to be treated quantum mechanically. Then the classical partition function has the form

$$Q(N, V, T) = \frac{q_{\text{intra}}^N}{\Lambda^{3N} N!} \int \prod_{i=1}^N d^3 \mathbf{r}_i \exp[-\beta U(\{\mathbf{r}_i\})], \quad (1.56)$$

where q_{intra} is the partition sum over all molecular energy levels

$$q_{\text{intra}} = \sum_i \exp(-\beta \epsilon_i). \quad (1.57)$$

It often has the form

$$q_{\text{intra}} = q_{\text{vib}} q_{\text{rot}} q_{\text{elec}}. \quad (1.58)$$

1.10 Classical Ideal Gas

Consider classical ideal gas, where there is no interaction between particles. The Hamiltonian of the system is given only by the kinetic energy contribution

$$H_{\text{ideal}}(\{\mathbf{r}_i, \mathbf{p}_i\}) = \sum_{i=1}^N \frac{p_i^2}{2m}. \quad (1.59)$$

Since there is no interaction between particles, $U = 0$, so the partition function is given by

$$Q_{\text{ideal}}(N, V, T) = \frac{1}{\Lambda^{3N} N!} \int \prod_{i=1}^N d\mathbf{r}_i = \frac{V^N}{\Lambda^{3N} N!}. \quad (1.60)$$

Hence,

$$A = -k_B T \ln Q_{\text{ideal}} = -k_B T \ln \left(\frac{V^N}{\Lambda^{3N} N!} \right), \quad (1.61)$$

and from the fundamental equation $dA = -PdV - SdT + \mu dN$, the expression for the pressure is

$$P_{\text{ideal}} = - \left(\frac{\partial A}{\partial V} \right)_{N,T} = \frac{Nk_B T}{V}. \quad (1.62)$$

This is the well-known ideal gas equation

$$pV = nRT. \quad (1.63)$$

1.11 Other Ensembles

There are five common ensembles that we usually consider

- (i) *Microcanonical (NVE) ensemble*: an isolated system;
- (ii) *Canonical (NVT) ensemble*: can exchange energy with the bath;
- (iii) *Isothermal-isobaric (NPT) ensemble*: can exchange both energy and volume with the bath;
- (iv) *Isoenthalpic-isobaric (NPH) ensemble*: can exchange volume with the bath;
- (v) *Grand canonical (μVT) ensemble*: can exchange particles and energy with the bath.

We have already considered microcanonical ensemble and canonical ensemble. Now let's consider an isothermal-isobaric ensemble: a system with N particles that can exchange energy and volume with a large reservoir. The probability finding the system at a given microstate $|i\rangle$ with energy E_i and volume V_i is determined by $\Omega_{\text{bath}}(E_{\text{tot}} - E_i, V_{\text{tot}} - V_i)$. By Taylor expansion as before, and using

$$\left(\frac{\partial S}{\partial E}\right)_{N,V} = \frac{1}{T}, \quad \left(\frac{\partial S}{\partial V}\right)_{E,N} = \frac{P}{T}, \quad (1.64)$$

we get

$$\ln \Omega_{\text{bath}}(E_{\text{tot}} - E_i, V_{\text{tot}} - V_i) = \ln \Omega_{\text{bath}}(E_{\text{tot}}, V_{\text{tot}}) - \frac{E_i + PV_i}{k_B T}. \quad (1.65)$$

The probability of finding the system with volume V is therefore given by

$$P(V) = \frac{Q(N, V, T) e^{-\beta PV}}{\Delta}, \quad (1.66)$$

where Δ is the *isothermal-isobaric partition function* quantum mechanically defined as

$$\Delta := \sum_{|i\rangle} Q(N, V, T) e^{-\beta PV}. \quad (1.67)$$

Classically, it is defined as

$$\Delta := \beta P \int_0^\infty dV Q(N, V, T) e^{-\beta PV}, \quad (1.68)$$

where βP is to make the quantity dimensionless, and correspondingly

$$P(V) = \frac{\beta P Q(N, V, T) e^{-\beta PV}}{\Delta}. \quad (1.69)$$

Then we have the bridge relationship

$$G = -k_B T \ln \Delta. \quad (1.70)$$

Another ensemble of great importance is the grand canonical ensemble. Consider a system of volume V that can exchange particles and energy with the reservoir. The probability finding N particles in the system in a state with energy E_i is determined by $\Omega_{\text{bath}}(E_{\text{tot}} - E_i, N_{\text{tot}} - N_i)$. Using

$$\left(\frac{\partial S}{\partial N}\right)_{E,V} = -\frac{\mu}{T}, \quad (1.71)$$

we get

$$P(N) = \frac{Q(N, V, T) \exp(\beta \mu N)}{\Xi}, \quad (1.72)$$

where

$$\Xi := \sum_{N=0}^{\infty} Q(N, V, T) \exp(\beta \mu N) \quad (1.73)$$

is the *grand partition function*. Then the *grand potential*, defined as

$$\Phi = E - TS - N\mu = -PV, \quad (1.74)$$

if related to the grand partition function by the bridge relation

$$\Phi = -k_B T \ln \Xi. \quad (1.75)$$

The average number of particles in the system is

$$\langle N \rangle = \left(\frac{\partial \ln \Xi}{\partial \beta \mu} \right)_{V,T}. \quad (1.76)$$

<i>microcanonical ensemble</i> constant N, V, E	<i>canonical ensemble</i> constant N, V, T
$S = k_B \ln \Omega(N, V, E)$	$A = E - TS = -k_B T \ln Q(N, V, T)$
$dE = -PdV + TdS + \mu dN$	$dA = -PdV - SdT + \mu dN$
$(1/T) = (\partial S / \partial E)_{N,V}$	$E = (\partial(\beta A) / \partial \beta)_{N,V}$
$P = T(\partial S / \partial V)_{E,N}$	$P = -(\partial A / \partial V)_{N,T}$
$\mu = -T(\partial S / \partial N)_{E,V}$	$\mu = (\partial A / \partial N)_{V,T}$
<i>isothermal-isobaric ensemble</i> constant N, P, T	<i>grand canonical ensemble</i> constant μ, V, T
$G = A + PV = N\mu = -k_B T \ln \Delta(N, P, T)$	$\Phi = A - \mu N = -PV = -k_B T \ln \Xi(\mu, V, T)$
$dG = VdP - SdT + \mu dN$	$d\Phi = -PdV - SdT - Nd\mu$
$H = E + PV = (\partial(\beta G) / \partial \beta)_{N,P}$	$N = -(\partial \Phi / \partial \mu)_{V,T}$
$V = (\partial G / \partial P)_{N,T}$	$P = -(\partial \Phi / \partial V)_{T,\mu}$
$\mu = (\partial G / \partial N)_{P,T}$	$E = N\mu + (\partial(\beta \Phi) / \partial \beta)_{\mu,V}$

It is possible to generate a lot more different ensembles by different combinations of Legendre transforms; however, the microcanonical, canonical and grand canonical ensembles are the most important ones.

1.11.1 Langmuir Adsorption

Why do we need different ensembles? In fact we will show that in the thermodynamic limit, all the ensembles are equivalent. However, some calculations may be more difficult in one ensemble than another. The choice of ensemble is primarily a matter of convenience.

As an illustration, consider the adsorption of gas molecules on the metal surface. Assume the metal has M sites, each can accommodate one molecule at most, and if a particle is adsorbed, its energy is lowered by ϵ . The gas has chemical potential μ .

First let's solve this question in canonical ensemble. If N particles are absorbed, the energy of the system is

$$E(N) = -N\epsilon, \quad (1.77)$$

and the degeneracy of this energy of the system is

$$\Omega(N) = \frac{M!}{N!(M-N)!}. \quad (1.78)$$

The canonical partition function is therefore

$$Q(N, M, T) = \frac{M!}{N!(M-N)!} \exp(\beta N \epsilon). \quad (1.79)$$

The chemical potential is

$$\mu = -k_B T \frac{\partial \ln Q}{\partial N} = -\epsilon + k_B T (\ln N - \ln(M-N)) \quad (1.80)$$

by Stirling's approximation. Define the density of adsorbed particles as $\rho := N/M$, then

$$\mu + \epsilon = k_B T \ln\left(\frac{\rho}{1-\rho}\right). \quad (1.81)$$

By rearranging, we get

$$\rho = \frac{1}{1 + \exp[-\beta(\mu + \epsilon)]}. \quad (1.82)$$

Now let's derive the same result in the grand canonical ensemble.

$$\Xi = \sum_{N=0}^M \frac{M!}{N!(M-N)!} \exp[N\beta(\mu + \epsilon)] \quad (1.83)$$

$$= (1 + \exp[\beta(\mu + \epsilon)])^M \quad (1.84)$$

by the binomial theorem. The average number of particles is therefore

$$\langle N \rangle = \left(\frac{\partial \ln \Xi}{\partial \beta \mu} \right)_{M,T} = \frac{M \exp[\beta(\mu + \epsilon)]}{1 + \exp[\beta(\mu + \epsilon)]}. \quad (1.85)$$

It immediately follows that

$$\langle \rho \rangle = \frac{1}{1 + \exp[-\beta(\mu + \epsilon)]} \quad (1.86)$$

as calculated before.

1.12 Pressure of Interacting Particles

1.12.1 Pressure from the Partition Function

Consider a system of interacting gas particles in a cubic box with edge length $L = V^{1/3}$. Define the scaled coordinate

$$\mathbf{s}_i = \frac{\mathbf{r}_i}{L}, \quad (1.87)$$

so that each component of \mathbf{s}_i ranges between zero and unity. We can then write

$$Q(N, V, T) = \frac{V^N}{\Lambda^{3N} N!} \int_0^1 \cdots \int_0^1 \prod_{i=1}^N d^3 \mathbf{s}_i \exp[-\beta U(\{\mathbf{s}_i\}, L)], \quad (1.88)$$

where we have included L as the parameter of U to indicate that U depends on the real rather than the scaled distances between the particles. The pressure is therefore

$$P = k_B T \left(\frac{\partial \ln V^N}{\partial V} \right)_{T,N} + k_B T \left(\frac{\partial}{\partial V} \ln \int_0^1 \cdots \int_0^1 \prod_{i=1}^N d^3 \mathbf{s}_i \exp[-\beta U(\{\mathbf{s}_i\}; L)] \right)_{T,N} \quad (1.89)$$

$$= \frac{Nk_B T}{V} - \frac{1}{\int \prod_{i=1}^N d^3 \mathbf{s}_i \exp[-\beta U(\{\mathbf{s}_i\}; L)]} \int \prod_{i=1}^N d^3 \mathbf{s}_i \exp[-\beta U(\{\mathbf{s}_i\}; L)] \frac{\partial U(\{\mathbf{s}_i\}; L)}{\partial V} \quad (1.90)$$

$$= \underbrace{\frac{Nk_B T}{V}}_{\text{ideal}} - \underbrace{\left\langle \frac{\partial U(\{\mathbf{s}_i\}; L)}{\partial V} \right\rangle}_{\text{non-ideal}}. \quad (1.91)$$

We now use the chain rule

$$\frac{\partial U(\{\mathbf{s}_i\}; L)}{\partial V} = \sum_{i=1}^N \sum_{j=1}^3 \frac{\partial U(\{\mathbf{s}_i\}; L)}{\partial r_{ij}} \frac{\partial r_{ij}}{\partial V}, \quad (1.92)$$

where $j \in \{1, 2, 3\}$. We have

$$\frac{\partial r_{ij}}{\partial V} = L \frac{\partial s_{ij}}{\partial V} = s_{ij} \frac{\partial V^{1/3}}{\partial V} = \frac{s_{ij}}{3V^{2/3}} = \frac{r_{ij}}{3V}. \quad (1.93)$$

Hence

$$\frac{\partial U(\{\mathbf{s}_i\}; L)}{\partial V} = \sum_{i=1}^N \sum_{j=1}^3 \frac{\partial U(\{\mathbf{s}_i\}; L)}{\partial r_{ij}} \frac{r_{ij}}{3V}. \quad (1.94)$$

For conservative forces, $\mathbf{f} = -\nabla U$, so

$$\frac{\partial U(\{\mathbf{r}_i\})}{\partial r_{ij}} = -f_{ij}. \quad (1.95)$$

Therefore,

$$P = \frac{Nk_B T}{V} + \frac{1}{3V} \left\langle \sum_{i=1}^N \mathbf{f}_i \cdot \mathbf{r}_i \right\rangle. \quad (1.96)$$

1.12.2 Pressure for Pairwise-additive Forces

Consider the special case that the intermolecular forces are pairwise-additive such that

$$\mathbf{f}_i = \sum_{j \neq i} \mathbf{f}_{ij}, \quad (1.97)$$

where \mathbf{f}_{ij} is the force on particle i exerted by particle j . Then

$$P = \frac{Nk_B T}{V} + \left\langle \sum_{i=1}^N \sum_{j \neq i} \frac{1}{3V} \mathbf{r}_i \cdot \mathbf{f}_{ij} \right\rangle. \quad (1.98)$$

If we permute the dummy indices i and j , we get

$$P = \frac{Nk_B T}{V} + \left\langle \sum_{j=1}^N \sum_{i \neq j}^N \frac{1}{3V} \mathbf{r}_j \cdot \mathbf{f}_{ji} \right\rangle. \quad (1.99)$$

By Newton's third law, we get

$$P = \frac{Nk_B T}{V} + \frac{1}{6V} \left\langle \sum_{j=1}^N \sum_{i \neq j}^N \mathbf{r}_{ij} \cdot \mathbf{f}_{ij} \right\rangle, \quad (1.100)$$

where $\mathbf{r}_{ij} := \mathbf{r}_i - \mathbf{r}_j$. This can be rewritten in the dimensionless form as

$$Z := \frac{PV}{Nk_B T} = 1 + \frac{1}{6k_B T} \left\langle \sum_{i \neq j} \mathbf{r}_{ij} \cdot \mathbf{f}_{ij} \right\rangle, \quad (1.101)$$

where Z is the *compressibility factor*. For an ideal gas, $Z = 1$.

1.13 Law of Corresponding States

If the interactions between the molecules are pairwise-additive, then the potential energy $U(\{\mathbf{r}_i\})$ can be written as

$$U(\{\mathbf{r}_i\}) = \frac{1}{2} \sum_{j=1}^N \sum_{i \neq j}^N \phi(r_{ij}). \quad (1.102)$$

The figure below shows two simple examples of pair potentials. The hard-sphere potential is usually used to describe the interactions between uncharged colloids, and the Lennard-Jones potential is often used to describe the interaction between atoms or simple (nearly spherical) molecules. At distance less than effective molecular diameter σ , the intermolecular pair potential is harshly repulsive. This is a consequence of Pauli principle. At large distances $r \gg \sigma$, the London dispersion forces take over, the strength of which decays as $1/r^6$. The Lennard-Jones potential provides a convenient interpolation between the short-range repulsion and the long-range attraction. It is of the form

$$\phi(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right]. \quad (1.103)$$

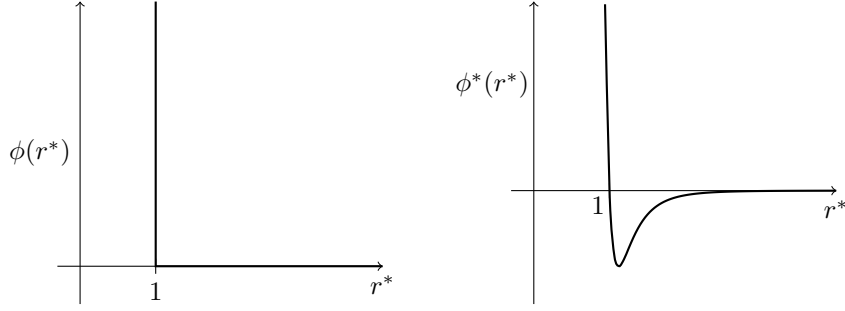
The depth of the potential is ϵ , whilst the range of the potential is determined by the effective diameter σ . Define $r^* := r/\sigma$ and $\phi^* := \phi/\epsilon$, then

$$\phi^*(r^*) = u_{LJ}(r^*) := 4 \left[r^{*12} - r^{*6} \right]. \quad (1.104)$$

Therefore, if we express all energies in units of ϵ and distances in units of σ , then all Lennard-Jones potentials are identical.

Using this definition, we can rewrite the compressibility in terms of the reduced quantities r^* and $f_{ij}^* := f_{ij}\sigma/\epsilon$, giving

$$Z = 1 + \frac{\epsilon}{6k_B T} \left\langle \sum_{i \neq j} \mathbf{r}_{ij}^* \cdot \mathbf{f}_{ij}^* \right\rangle \quad (1.105)$$



Now define the reduced temperature $T^* := k_B T / \epsilon$ and the reduced density $\rho^* := \sigma^3 N / V$, then

$$Z(\rho^*, T^*) = 1 + \frac{1}{6T^*} \left\langle \sum_{i \neq j} \mathbf{r}_{ij}^* \cdot \mathbf{f}_{ij}^* \right\rangle. \quad (1.106)$$

This equation implies that if we express the temperature in units of ϵ/k_B and density in units of σ^{-3} , then the compressibility factors of all substances that can be described by a pair potential in the same functional form collapse onto the same set of curves. This is known as the principle of corresponding states.

We can rewrite the above expression explicitly in terms of ρ^* . We have

$$P = \frac{Nk_B T}{V} + \frac{N}{6V} \left\langle \sum_{i \neq j} \mathbf{r}_{ij} \cdot \mathbf{f}_{ij} \right\rangle, \quad (1.107)$$

which can be written in reduced quantity as

$$P^* = \rho^* T^* + \frac{\rho^*}{6} \left\langle \sum_{i \neq j} \mathbf{r}_{ij}^* \cdot \mathbf{f}_{ij}^* \right\rangle. \quad (1.108)$$

We then have

$$\left\langle \sum_{i \neq j} \mathbf{r}_{ij}^* \cdot \mathbf{f}_{ij}^* \right\rangle = \frac{6(P^* - \rho^* T^*)}{\rho^*}. \quad (1.109)$$

Hence the compressibility factor is

$$Z = 1 + \frac{1}{6T^*} \frac{P^* - \rho^* T^*}{\rho^*} \quad (1.110)$$

$$= \frac{P^*}{\rho^* T^*}. \quad (1.111)$$

2 Free Energy and Phase Behaviour

2.1 Equilibrium between Phases

Consider an isolated system of N particles in a volume V with a total energy E . The system consists of multiple distinct phases between which particles, volume and energy can be exchanged. We ignore any contributions of the interfaces to the extensive properties, as their contribution scales as $N^{2/3}$, so their ratio compared with bulk contribution scales as $N^{-1/3}$, vanishing in the thermodynamic limit as $N \rightarrow \infty$. Then the equilibrium conditions of coexistence of phases are that the pressures of all coexisting phases must be equal ($P_1 = P_2 = \dots = P$), as must be the temperature ($T_1 = T_2 = \dots = T$) and the chemical potentials of all species ($\mu_1^\alpha = \mu_2^\alpha = \dots = \mu^\alpha$).

2.1.1 Stability

We use the thermodynamic arguments to find conditions for the stability of a single phase. Consider a homogeneous phase in an isolated system with constant N , V and E that is divided into two equal halves. At equilibrium, the entropy of the total system is at a maximum. Now consider transferring a small amount of energy ΔE from one half of the system to the other. At equilibrium, the temperature in the two halves of the system is the same, and hence to linear order of ΔE , the entropy does not change. Consider the second order variation,

$$\Delta S = \frac{1}{2} \left(\frac{\partial(1/T)}{\partial E} (\Delta E)^2 \right)_1 + \frac{1}{2} \left(\frac{\partial(1/T)}{\partial E} (\Delta E)^2 \right). \quad (2.1)$$

Since the two halves of the system are identical, these two terms are the same. We can write

$$\Delta S = \frac{\partial(1/T)}{\partial E} (\Delta E)^2. \quad (2.2)$$

As S is a maximum, $\Delta S \leq 0$, and hence

$$\frac{\partial E}{\partial(1/T)} \leq 0, \quad (2.3)$$

which implies that

$$-T^2 \frac{\partial E}{\partial T} = -T^2 C_V \leq 0, \quad (2.4)$$

and hence the heat capacity $C_V \geq 0$. Thermodynamic stability implies that the heat capacity is never negative.

A similar argument can be used to show that the compressibility of a system is non-negative. Consider the condition for equilibrium at constant N , V and T . Under these conditions, the Helmholtz energy must be a minimum. We divide the system into two equal parts, both containing $N/2$ particles in a volume $V/2$ at constant T . We now vary the volume of one half of the system by an amount ΔV , and the other by $-\Delta V$. To first order in ΔV , the total variation of the free energy is

$$\Delta A = \frac{\partial^2 A}{\partial V^2} (\Delta V)^2. \quad (2.5)$$

This can be rewritten as

$$\Delta A = -\frac{\partial P}{\partial V}(\Delta V)^2 = \frac{1}{\kappa V}(\Delta V)^2, \quad (2.6)$$

where κ is the isothermal compressibility of the system. As A is minimised at equilibrium, this implies that $\kappa \geq 0$.

2.2 Coexistence

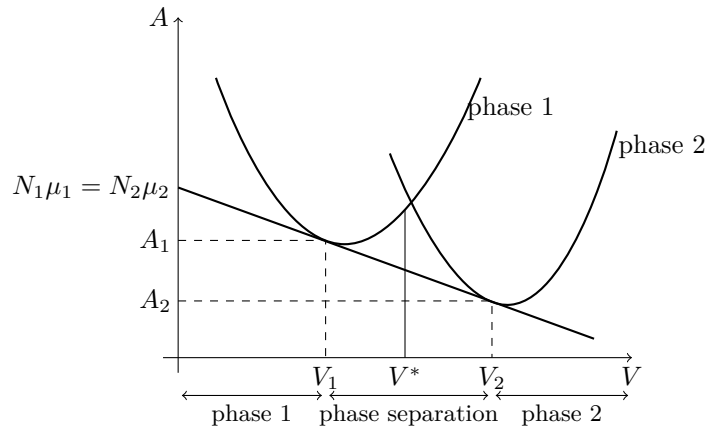
Consider a con-component system that can exist in two phases, with free energies $A_1(N, V, T)$ and $A_2(N, V, T)$. We would like to determine the condition that the two phase coexists. It turns out that there is a easy graphical method to do this. For a given temperature, we plot $A_1(N, V, T)$ and $A_2(N, V, T)$ as a function of V while keeping N and T constant. We now have to check if it is possible to draw a line that is tangent of both curves. If this common tangent exists, then this line touches A_1 at volume V_1 and it touches A_2 at a volume V_2 . As the curves A_1 and A_2 has a common tangent, the derivatives of A_1 and A_2 at V_1 and V_2 , respectively, are the same. As $(\partial A/\partial V)_T = -P$, this implies that the pressure of phase 1 at V_1 is the same of that of phase 2 at V_2 , i.e. $P_1 = P_2$. The tangents also have a common intercept at $V = 0$. This intercept is

$$A_1 - \frac{\partial A_1}{\partial V}V_1 = A_1 + PV_1 = G_1 = N\mu_1, \quad (2.7)$$

and this is equal to

$$A_2 - \frac{\partial A_2}{\partial V}V_2 = A_2 + PV_2 = G_2 = N\mu_2. \quad (2.8)$$

Therefore $\mu_1 = \mu_2$ and the volumes V_1 and V_2 are the volumes of the coexisting phases. A completely analogous analysis can be performed if we plot A/V against N/V , in which case the slope is related to the chemical potential and the intercept is related to the pressure.



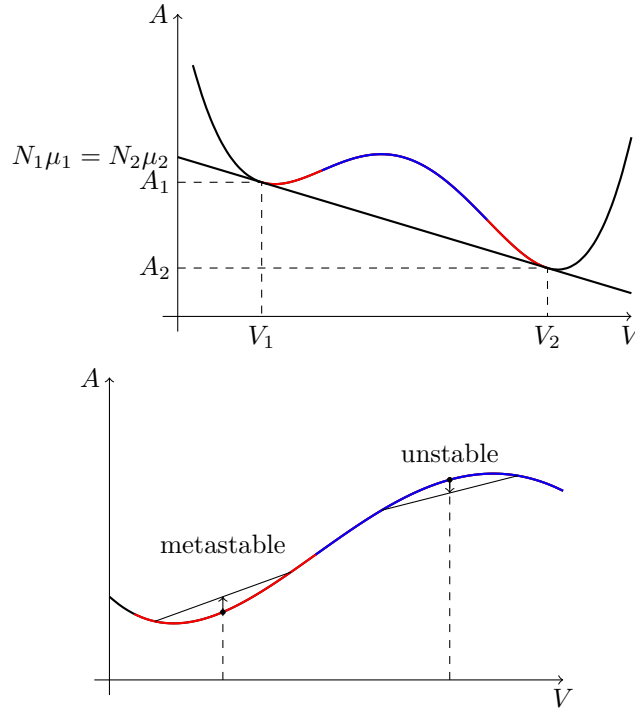
If the system is at some volume V^* with $V_1 \leq V^* \leq V_2$, the system would have lower Helmholtz energy if it is separated into the two phases than if it exists in either of the single phase. Define $v := V/N$, then

$$Nv^* = N_1v_1 + (N - N_1)v_2. \quad (2.9)$$

We can then derive the proportion of particles being in phase 1 at equilibrium

$$x_1 := \frac{N_1}{N} = \frac{v^* - v_2}{v_1 - v_2}. \quad (2.10)$$

Suppose now we have a free energy curve for some phase. We have shown that the free energy must be a convex function of V because the compressibility κ must be non-negative at equilibrium. Hence, the non-convex part in curve A versus V does not correspond to an equilibrium situation. We can still work out the point of coexistence by common tangent construction. But now we have a region where the phase separation is thermodynamically favourable, but the local second derivative of A with respect to V is still positive, meaning that any perturbation of such system will increase the free energy. Such system is described as meta-stable as phase separation will involve a free-energy barrier. Between the inflection points, the free energy curve is non-convex and hence in this range a homogeneous phase would be absolutely unstable, with a negative compressibility. Such a system will phase separate spontaneously under any infinitesimal fluctuation. The boundary between the metastable and unstable regions are called *spinodal*.



It should be stressed that the spinodal, although a useful qualitative concept, is not well defined. It appears naturally when we use approximate expressions for the free energy. However, an exact expression for the equilibrium free energy is necessarily convex and therefore has no spinodal.

2.3 Phase Diagrams

A phase diagrams can tell us at a glance the conditions under which each phase is thermodynamically stable. For a one-component system, the thermodynamic variables

P , T and V , which are usually used to describe the thermodynamic state of the matter, are not independent of one another. For example, if we specify the volume and the temperature of a system, the pressure will be defined as well through the equation of states. We can therefore think of the phase diagram as a surface in the PVT space. Such a three-dimensional phase diagram can be projected onto the $P - T$, $V - T$, $P - V$ or $T - \rho$ planes to give the more familiar two-dimensional phase diagrams.

There are many other parameters that we could vary; for example we could change the composition of a mixture or the strength of an external magnetic field, and so other types of phase diagrams can be constructed, some of which we shall see in the chapters that follow.

2.4 Thermodynamic Integration

The second law of thermodynamics states that for an isolated system with energy E , volume V and number of particles N , the entropy S is maximised when the system is at equilibrium. From this formulation of the second law, it is straightforward to derive the corresponding equilibrium conditions for systems that can exchange heat, particles or volume with a reservoir, as we have already shown. In particular, if a system is in contact with a heat bath, such that its temperature T , volume V and number of particles N are fixed, then the Helmholtz energy $A := E - TS$ is at a minimum in equilibrium. Analogously, for a system of N particles at constant pressure P and temperature T , the Gibbs energy $G := A + PV$ is at a minimum.

If we wish to know which of two phases, denoted 1 and 2, is stable at a given temperature and density, we simply need to compare the Helmholtz energies A_1 and A_2 . Unfortunately, it is not possible to measure the free energy or entropy directly. What we can measure are averages of *mechanical quantities*, i.e. averages of functions of the coordinates and momenta of the molecules in the system, such as the pressure or the dielectric constant. If we denote such a mechanical quantity by $X(\{\mathbf{p}_i\}, \{\mathbf{r}_i\})$, then the average of X that can be measured in an experiment at constant N , V and T is

$$\langle X \rangle_{NVT} = \frac{\int \prod_{i=1}^N d^3\mathbf{p}_i d^3\mathbf{r}_i X(\{\mathbf{p}_i\}, \{\mathbf{r}_i\}) \exp[-\beta H(\{\mathbf{p}_i\}, \{\mathbf{r}_i\})]}{\int \prod_{i=1}^N d^3\mathbf{p}_i d^3\mathbf{r}_i \exp[-\beta H(\{\mathbf{p}_i\}, \{\mathbf{r}_i\})]}, \quad (2.11)$$

where $H(\{\mathbf{p}_i\}, \{\mathbf{r}_i\})$ is the system's Hamiltonian.

However, the entropy, the free energy and related quantities are not simply averages of functions of the phase-space coordinates of the system. Rather, they are directly related to the volume in phase space that is accessible to a system. For instance, in classical statistical mechanics, the Helmholtz energy A is directly related to the canonical partition function $Q(N, V, T)$ through

$$\begin{aligned} A &= -k_B T \ln Q(N, V, T) \\ &= -k_B T \ln \left[\frac{1}{h^{3N} N!} \int \prod_{i=1}^N d^3\mathbf{p}_i d^3\mathbf{r}_i \exp[-\beta H(\{\mathbf{p}_i\}, \{\mathbf{r}_i\})] \right]. \end{aligned} \quad (2.12)$$

Unlike quantities such as the internal energy the pressure or the polarisation,

$Q(N, V, T)$ itself is not a canonical average over the phase space. This is why A and, for that matter, S or G , cannot be measured directly. We call quantities that depend directly on the available volume in the phase space *thermal quantities*. However, derivatives of the free energy with respect to the volume V or the temperature T are mechanical quantities and can be measured: namely, they are

$$\left(\frac{\partial A}{\partial V}\right)_{N,T} = -P \text{ and } \left(\frac{\partial(A/T)}{\partial(1/T)}\right)_{V,T} = E. \quad (2.13)$$

In order to compute the free energy of a system at a given temperature and density, we must find a reversible path in the volume-temperature plane that links the state under consideration to a state of known free energy. Then change in A along that path can then be simply be evaluated by integrating (2.13). Only a few thermodynamic states exist whose free energy is known exactly: one such state in the ideal gas; another may be perfectly ordered ground state at $T = 0$ K.

3 Thermodynamic Perturbation Theory

3.1 Gibbs–Bogoliubov Relation

The aim of thermodynamic perturbation theory is to arrive at an estimate of the free energy (and all derived properties) of a many-body system, using as input information about the free energy and structure of a simpler reference system. We assume that the potential energy function of this reference system is denoted by U_0 , while the potential energy function of the system of interest is denoted by U_1 . In order to compute the free-energy difference between the known reference system and the system of interest, we use a linear parameterisation of the potential energy function

$$U(\lambda) := \lambda U_1 + (1 - \lambda)U_0. \quad (3.1)$$

The free energy of a system with this generalised potential energy is denoted $A(\lambda)$ and can be computed from $A(\lambda) = -k_B T \ln Q(\lambda)$. In particular, we noted when introducing (2.13) that derivatives of the free energy are often mechanical observables, and the same applies in this case. The derivative of $A(\lambda)$ with respect to λ is

$$\left(\frac{\partial A}{\partial \lambda}\right)_{NVT} = \frac{\int \prod_{i=1}^N d^3 \mathbf{r}_i \left(\frac{\partial U(\{\mathbf{r}_i\}; \lambda)}{\partial \lambda}\right) \exp[-\beta U(\{\mathbf{r}_i\}; \lambda)]}{\int \prod_{i=1}^N d^3 \mathbf{r}_i \exp[-\beta U(\{\mathbf{r}_i\}; \lambda)]} \quad (3.2)$$

$$= \left\langle \frac{\partial U(\lambda)}{\partial \lambda} \right\rangle_{\lambda} \quad (3.3)$$

$$= \langle U_1 - U_0 \rangle_{\lambda}, \quad (3.4)$$

and hence we can express the free-energy difference $A_1 - A_0$ as

$$A_1 - A_0 = \int_0^1 d\lambda \langle U_1 - U_0 \rangle_{\lambda}, \quad (3.5)$$

where the subscript λ indicates that we evaluate the thermal average of the value of λ . This expression, first derived by John Kirkwood in 1935, allows us to compute

the free energy of a system of interest by relating it to a reference system. This approach has extensively been used in computer simulations since the mid-1980s. It is often referred to as ‘artificial’ or ‘Hamiltonian’ thermodynamic integration because it entails changing the underlying interactions in the system’s Hamiltonian.

Moreover, it allows us to find bounds on the free energy A_1 . It is straightforward to show that

$$\left(\frac{\partial^2 A}{\partial \lambda^2}\right)_{NVT} = -\beta (\langle (U_1 - U_0)^2 \rangle_\lambda - \langle U_1 - U_0 \rangle_\lambda^2) \leq 0. \quad (3.6)$$

Since the right-hand side of the equation is the negative of a variance, we can note that the second derivative of A with respect to λ is always non-positive. This implies that

$$\left(\frac{\partial A}{\partial \lambda}\right)_{\lambda=0} \geq \left(\frac{\partial A}{\partial \lambda}\right)_{\lambda>0}, \quad (3.7)$$

and hence

$$A_1 \leq A_0 + \langle U_1 - U_0 \rangle_\lambda. \quad (3.8)$$

This variational principle for the free energy is known as the *Gibbs-Bogoliubov inequality*: we compute an upper bound to the free energy of the system of interest from a knowledge of the average of $U_1 - U_0$ evaluated for the reference system. The latter is something that can often be computed because the reference system is by construction a system which we can solve.

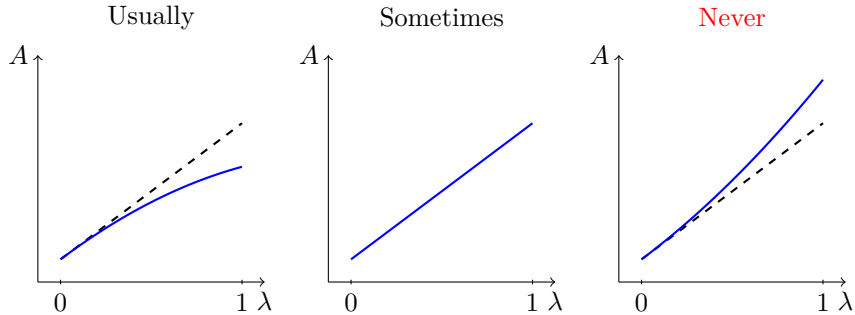


Figure 3.1: The Gibbs-Bogoliubov inequality shows that the first order perturbation estimation of the free energy is never lower than the true free energy.

We may let of reference system depend on some parameters and use the variational principle the get our best estimation of the upper bound of Helmholtz energy.

It may seem at first glance that we are doing something slightly off here: what does it actually mean that we compute $\langle U_1 \rangle_{\lambda=0}$ for the reference potential, given that when $\lambda = 0$, the system is governed by U_0 only? In this case, U_1 does not contribute to the Boltzmann factor, but that does not mean we are not able to compute what it is for a given microstate, since it depends only on the momenta of a given microstate. This is similar to computing any other mechanical observable, e.g. the pressure, which also would not appear in the Boltzmann factor. It is evaluated as

$$\langle U_1 - U_0 \rangle_{\lambda=0} = \frac{\int \prod_{i=1}^N d^3 \mathbf{r}_i U_0 \exp(-\beta U_0)}{\int \prod_{i=1}^N d^3 \mathbf{r}_i U_0 \exp(-\beta U_0)}. \quad (3.9)$$

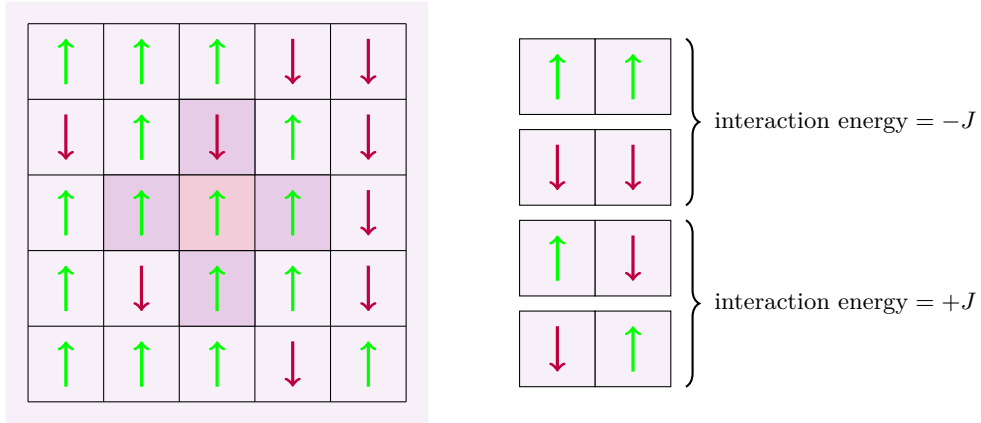


Figure 3.2: A schematic representation of the Ising model in two dimensions.

The usefulness of (3.8) depends crucially on the quality of the choice of reference system. A good reference system is not necessarily close in free energy to the system of interest, but one for which the fluctuation in the potential energy difference $U_1 - U_0$ are small. Thermodynamic perturbation theory for simple liquids has been very successfully precise because the structure of the reference system (hard-sphere fluid) and the liquid under consideration (e.g. Lennard-Jones) are very similar. As a result, $\langle U_1 - U_0 \rangle_\lambda$ hardly depends on λ and, as a consequence, its derivative is small.

3.2 Mean-Field Theory and the Ising Model

The Gibbs-Bogoliubov inequality can be used as a starting point from which we can derive mean-field theory, which provides a systematic approximation to the free energy of a many-body system. For the sake of simplicity, we consider the Ising model, for which a many-body Hamiltonian of N interacting spins is given by

$$U_1 = -\frac{J}{2} \sum_{i=1}^N \sum_{\langle i,j \rangle} s_i s_j, \quad (3.10)$$

where $\langle i,j \rangle$ indicates that the particles j must be nearest neighbours of i and the factor of $1/2$ ensures that we do not double count the interactions. The Ising model is not just relevant for magnetic systems; in ??, we show that a lattice-gas model that can be used to describe the liquid-vapour transition is, in fact, equivalent to the Ising model.

We wish to approximate this model system using a reference system with a much simpler Hamiltonian, namely one that consists only of a sum of one-particle contributions. For example,

$$U_0 = -\sum_{i=1}^N h s_i, \quad (3.11)$$

where h denotes the effective field that replaces the interaction with the other particles. The molecular partition function counting all states of a single spin (with energy $-hs$)

in the reference system is

$$q_0 = \int d^s \exp(\beta h s) \quad (3.12)$$

and the free energy per spin is

$$a_0(h) = -k_B T \ln q_0 = -k_B T \ln \int d^s \exp(\beta h s). \quad (3.13)$$

Here, we use the shorthand a for A/N . If the spins are quantised and we only have two spin states (+1 and -1), the partition function reduces to

$$q_0 = \exp(\beta h) + \exp(-\beta h) = 2 \cosh(\beta h) \quad (3.14)$$

and the free energy becomes

$$a_0(h) = -k_B T \ln(2 \cosh(\beta h)). \quad (3.15)$$

We can easily compute the average value of s in the reference system,

$$\langle s \rangle_0 = \frac{\int d^s s \exp(\beta h s)}{q_0} = \frac{1}{q_0} \frac{\partial}{\partial \beta h} \int d^s \exp(\beta h s) = k_B T \frac{\partial \ln q_0}{\partial h}, \quad (3.16)$$

or simply

$$\langle s \rangle_0 = -\frac{\partial a_0(h)}{\partial h}. \quad (3.17)$$

In the case of spins ± 1 ,

$$\langle s \rangle_0 = \tanh(\beta h), \quad (3.18)$$

which we could have obtained directly from the definition of the mean magnetisation, but the expression involving the derivative of a_0 will come in useful shortly. Now, we consider the Gibbs–Bogoliubov inequality, where

$$a_{\text{MF}} = a_0 + \left\langle -\frac{J}{2} \sum_{\langle i,j \rangle} s_i s_j + h s_i \right\rangle_0 \quad (3.19)$$

$$= a_0 - \frac{J}{2} z \langle s \rangle_0^2 + h \langle s \rangle_0. \quad (3.20)$$

In the last line, we have introduced z , the coordination number of particle i . Moreover, we have used the fact that, in the reference system, different spins are uncorrelated, $\langle s_i s_j \rangle_0 = \langle s_i \rangle_0 \langle s_j \rangle_0$. We now look for the optimum value for h , i.e. the one that minimises our estimate of a_{MF} . Carrying out the differentiation with respect to h , we find that

$$0 = \frac{\partial}{\partial h} \left(a_0 - \frac{J}{2} z \langle s \rangle_0^2 + h \langle s \rangle_0 \right) \quad (3.21)$$

$$= -\langle s \rangle_0 - (Jz \langle s \rangle_0 - h) \frac{\partial \langle s \rangle_0}{\partial h} + \langle s \rangle_0 \quad (3.22)$$

$$= -(Jz \langle s \rangle_0 - h) \frac{\partial \langle s \rangle_0}{\partial h}. \quad (3.23)$$

Since $\frac{\partial \langle s \rangle_0}{\partial h} \neq 0$, we can conclude that

$$h = Jz \langle s \rangle_0. \quad (3.24)$$

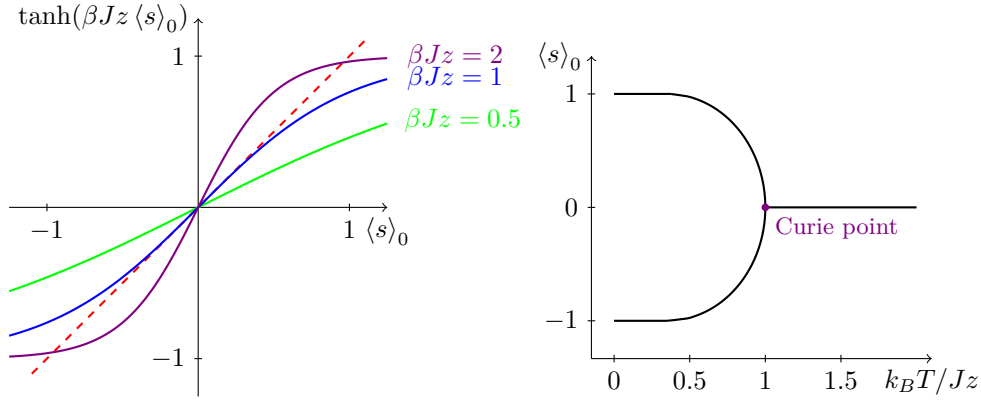


Figure 3.3: (a) A graphical method for the solution of the mean magnetisation in Ising model. (b) The phase diagram of an Ising model system.

Finally, we can insert this expression for h into (3.18) to obtain an implicit equation for $\langle s \rangle_0$,

$$\langle s \rangle_0 = \tanh(\beta J z \langle s \rangle_0), \quad (3.25)$$

which can be solved to yield $\langle s \rangle_0$ as a function of T .

Above the critical (or Curie) temperature, there is only one solution: at high temperatures, the entropy dominates the free energy and so the spins are randomly distributed. The significance of the entropy as a driving force is diminished as the temperature is decreased, and below the Curie temperature, the net alignment of spins, which is energetically favourable, becomes dominant, and the mean magnetisation per spin is non-zero. In fact, as can be seen from the figure, there are three solutions to the mean magnetisation. However, the $\langle s \rangle = 0$ solution is actually a maximum, rather than a minimum, so we will ignore it. In the absence of an external magnetic field, the system is equally likely to be magnetised in the up or the down spin configurations, but the fluctuations causing the transitions between the two are extremely unlikely. The ergodic hypothesis is thus formally violated, and this phenomenon is sometimes described as *spontaneous symmetry breaking*.

The free energy estimate that we obtain when inserting (3.24) into (3.20) is

$$a_{\text{MF}} = a_0 + \frac{J}{2} z \langle s \rangle_0^2. \quad (3.26)$$

The subscript ‘MF’ in this expression stands for the mean field approximation. It is very important to bear in mind that the free energy that results from the mean-field approximation is in general not simply the free energy of the reference system with the effective field, but has an additional term that depends on the difference between the two potentials measured for the system with the effective field.

3.3 Van der Waals Equation

In some cases, the fluctuation term in the Gibbs–Bogoliubov approach can be made to vanish altogether. A famous example of this occurring is the mean-field treatment

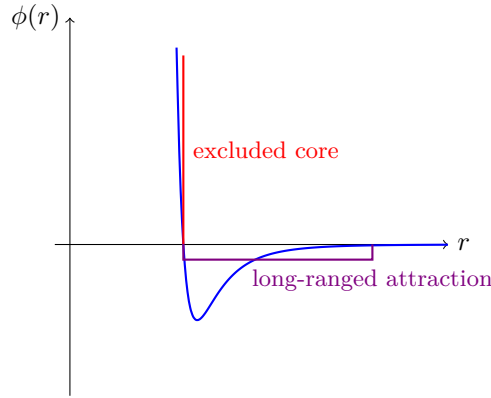


Figure 3.4: A typical interatomic potential (shown in blue) can be approximated by a hard-core repulsion and a very weak attractive interaction $-\epsilon$.

of the Van der Waals fluid, where we take a hard-sphere reference system and add a very weak, attractive interaction $-\epsilon$ that extends to a very large distance R_c . In order to compute the Van der Waals free energy, we first need to work out the equation of state of a hard-sphere gas. Unfortunately this proves to be the more challenging part of the calculation in this case.

3.3.1 Hard-Sphere Gas

The hard-sphere potential is given by

$$U_0 = \sum_{i < j} \phi(r_{ij}), \quad (3.27)$$

where

$$\phi(r_{ij}) = \begin{cases} 0 & \text{if } r_{ij} > \sigma \\ \infty & \text{if } r_{ij} \leq \sigma, \end{cases} \quad (3.28)$$

where σ is the diameter of the particle.

Provided the hard-sphere gas is sufficiently dilute, we can estimate that the addition of each additional hard sphere reduced the volume available to the next one by $v_{\text{ex}} = 4\pi\sigma^3/3$, the volume excluded by a single hard sphere. In the dilute limit, we estimate that no two excluded volumes will overlap. An illustration of this set-up is given in the figure below. In this case, we can simply modify the perfect gas partition function to give

$$Q_{\text{HS}} \approx \frac{1}{\Lambda^{3N} N!} V(V - v_{\text{ex}})(V - 2v_{\text{ex}}) \dots (V - (N - 1)v_{\text{ex}}) \quad (3.29)$$

$$= \frac{V^N}{\Lambda^{3N} N!} \left(1 - \frac{v_{\text{ex}}}{V}\right) \left(1 - 2\frac{v_{\text{ex}}}{V}\right) \dots \left(1 - (N - 1)\frac{v_{\text{ex}}}{V}\right). \quad (3.30)$$

In the dilute regime, $(N - 1)v_{\text{ex}}/V \ll 1$, so we can use the power series $\exp(-x) =$

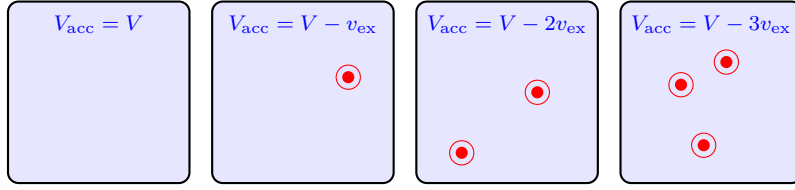


Figure 3.5: Ignoring any volume excluded by the walls and any excluded volume overlaps, each particle inserted into the system excludes a volume v_{ex} , reducing the accessible volume.

$1 - x$, giving

$$Q_{\text{HS}} = \frac{V^N}{\Lambda^{3N} N!} \exp\left(-\frac{v_{\text{ex}}}{V}\right) \exp\left(-\frac{2v_{\text{ex}}}{V}\right) \dots \exp\left(-\frac{(N-1)v_{\text{ex}}}{V}\right) \quad (3.31)$$

$$= \frac{V^N}{\Lambda^{3N} N!} \exp\left(-\frac{v_{\text{ex}}}{V} \sum_{i=1}^{N-1} i\right). \quad (3.32)$$

The summation is an arithmetic series that we can evaluate as $N(N-1)/2$. Since $Nv_{\text{ex}}/2V \ll 1$ by construction, we can ignore the linear term in the exponential and write

$$Q_{\text{HS}} \approx \frac{V^N}{\Lambda^{3N} N!} \exp\left(-\frac{N^2 v_{\text{ex}}}{2V}\right) = \frac{V^N}{\Lambda^{3N} N!} \left[\exp\left(-\frac{Nv_{\text{ex}}}{2V}\right) \right]^N. \quad (3.33)$$

If we use the same expansion again and if we note that $v_{\text{ex}} = 8v_0$, where v_0 is the volume of a single hard sphere particle, we obtain

$$Q_{\text{HS}} \approx \frac{(V - 4Nv_0)^N}{\Lambda^{3N} N!}. \quad (3.34)$$

Using $A = -k_B T \ln Q$, Stirling's approximation and $P = -(\partial A / \partial V)_{N,T}$, we can write

$$P_{\text{HS}} \approx \frac{Nk_B T}{V - 4Nv_0} = \frac{k_B T}{v_0} \frac{\phi}{1 - 4\phi}, \quad (3.35)$$

where in the last step we rewrote the volume in terms of the overall fraction of volume occupied, $\phi := Nv_0/V$. We note that this function diverges when $\phi \rightarrow 1/4$. In reality, hard spheres can be compressed to the close-packed volume fraction $\phi = \pi/\sqrt{18} \approx 0.7405$, and so the approximate partition function above is not appropriate at higher densities. This hard-sphere equation of state, and the corresponding Van der Waals equation of state that we will derive from it, are thus approximations that are only reasonable at low density.

3.3.2 Mean-Field Attractions

We have accounted for, in an approximated way, the hard-core repulsion between particles. We would now like to add the weak pairwise attraction $-\epsilon$. In particular, we consider the limit of very weak attractions ($\epsilon \rightarrow 0$) that are very long-range ($R_c \rightarrow \infty$). In this limit, the potential energy of the perturbed fluid can be computed directly. Within a shell of radius R_c , there will be, on average, $N_c = (4/3)\pi R_c^3 \rho$ other particles, where ρ is the number density of the fluid. All these particles contribute $-\epsilon/2$ to the

potential energy of the fluid, with the factor of $1/2$ accounting for the double-counting of pairwise interaction. For $R_c \rightarrow \infty$, the number of neighbours N_c also tends to infinity and hence the relative fluctuation in N_c becomes negligible, as it is of order $1/\sqrt{N_c}$. It then follows that the fluctuation in the perturbation (i.e. $U_1 - U_0$) also become negligible and, since we have shown that the second derivative of the free energy is proportional to the variance in $U_1 - U_0$, the first-order Maclaurin expansion of the free energy in λ becomes exact. Therefore the Gibbs-Bogoliubov inequality becomes an identity. The free energy per particle of the Van der Waals fluid is therefore

$$\left(\frac{A}{N}\right)_{\text{vdW}}(\rho, T) = \left(\frac{A}{N}\right)_{\text{HS}}(\rho, T) - \rho a, \quad (3.36)$$

where we have defined $a = (2\pi/3)R_c^3\epsilon$. The corresponding pressure is

$$P_{\text{vdW}} = - \left(\frac{\partial A_{\text{vdW}}}{\partial V} \right)_{N,T} = \rho^2 \frac{\partial (A/N)_{\text{vdW}}}{\partial \rho} = P_{\text{HS}}(\rho, T) - a^2 \rho, \quad (3.37)$$

where P_{HS} denotes the pressure of the hard-sphere reference system. We therefore have the well-known Van der Waals equation

$$(P_{\text{vdW}} + a\rho^2)(V - Nb) = Nk_B T, \quad (3.38)$$

where $b = 4v_0$. This equation is very interesting to study because it is probably the simplest model system which exhibits vapour-liquid coexistence. A simple way of computing the phase diagram involves the use of Maxwell's equal-area construction.

3.4 Maxwell Equal-Area Construction

We can sketch the behaviour of the pressure with volume above and below the critical point. Above the critical point, a single fluid phase exists; below the critical point, a vapour (low-density fluid) and a liquid (high-density fluid) are predicted. Below the critical point, there are regions where the equation of state describes a mechanically unstable state where the isothermal compressibility is negative, and where a single pressure corresponds to multiple possible volumes. Such regions are known as Van der Waals loops. The critical point itself occurs at the point at which the minimum and the maximum of the Van der Waals loop merge, i.e. the first and second derivatives of the pressure with respect to volume vanish.

In regions where there are Van der Waals loops, we can immediately find the points corresponding to limits of mechanical stability: these 'spinodals' correspond to the points at which $(\partial P / \partial V)$ changes sign. Finding the points of coexistence (the 'binodals') is slightly more challenging. Various approaches can be used; here, we will use a Maxwell construction.

We have already shown that the condition for phase equilibrium – in this case between the liquid and the vapour – is the equality of pressures, temperatures and chemical potentials. From our discussion of the common tangent construction approach, we know that the condition that the chemical potentials are equal is given by

$$N\mu_1 = N\mu_2 = A_1 + P_{\text{comm}}V_1 + A_2P_{\text{comm}}V_2, \quad (3.39)$$

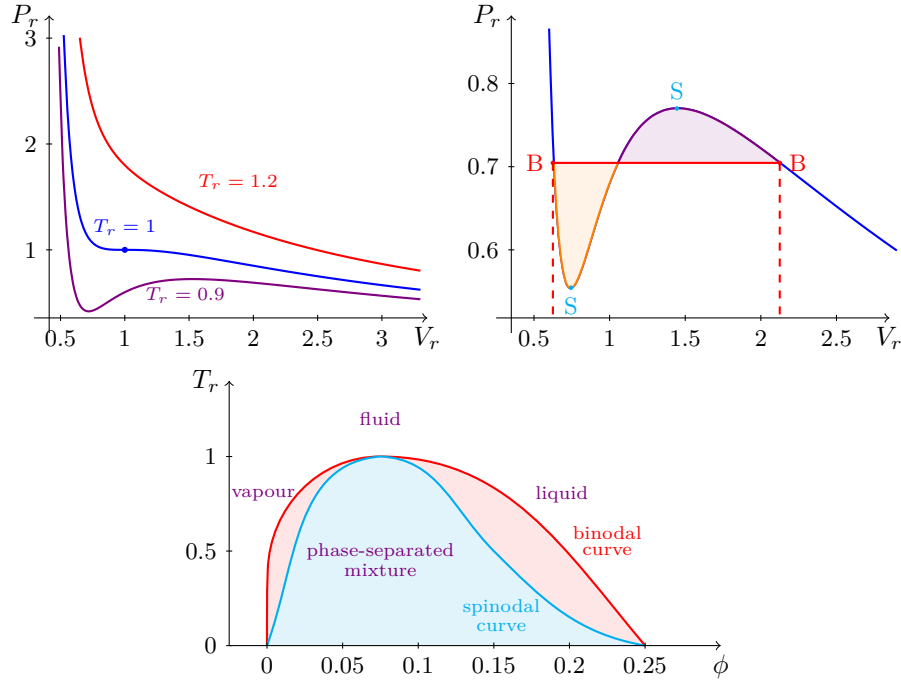


Figure 3.6: (a) The pressure as a function of the volume above, at and below the critical temperature. All quantities are scaled by their values at the critical point. (b) Below the critical point, the pressure has a ‘Van der Waals loop’. A Maxwell equal-area construction, shown here, is used to find the point of coexistence (labelled ‘B’). Spinodals, where the system becomes mechanically unstable, are labelled ‘S’. (c) Phase diagram for the Van der Waals model determined using Maxwell constructions.

where P is the common pressure. This is fulfilled if $P_{\text{comm}}(V_1 - V_2) = A_1 - A_2$.

We can also express the pressure as $P = -(\partial A / \partial V)_{N,T}$, and therefore, if we use thermodynamic integration, we find that

$$A_1 - A_2 = - \int_0^{V_1} dV P + \int_0^{V_2} dV P. \quad (3.40)$$

Hence the condition for coexistence is

$$P_{\text{comm}}(V_2 - V_1) = \int_{V_1}^{V_2} dV P. \quad (3.41)$$

This condition means that the area of the rectangle spanned by V_1 and V_2 along the volume axis and 0 and P_{comm} along the pressure axis is equal to the area under the P curve between V_1 and V_2 . As can be seen in the figure, the only difference between the two areas is the region where area 1 carves an area into the rectangle and area 2 protrudes from the rectangle: to satisfy (3.41), we simply require that area 1 should equal area 2. In practice, we need to vary P_{comm} until the two areas match. A phase diagram corresponding to the Van der Waals equation of state is shown in the figure.

We used an approximate equation of state for a hard-sphere gas in our derivation, and so, as we argued above, the Van der Waals equation of state is also only reasonable at low density. If, on the other hand, we use the exact equation of state of hard spheres as deduced from computer simulations, then we can compute the ‘exact’ equation of

state of the Van der Waals model (i.e. the equation of state that Van der Waals would have given an arm and a leg for). Using this approach, Longuet-Higgins and Widom were the first to compute the true phase diagram of the Vander Waals model.

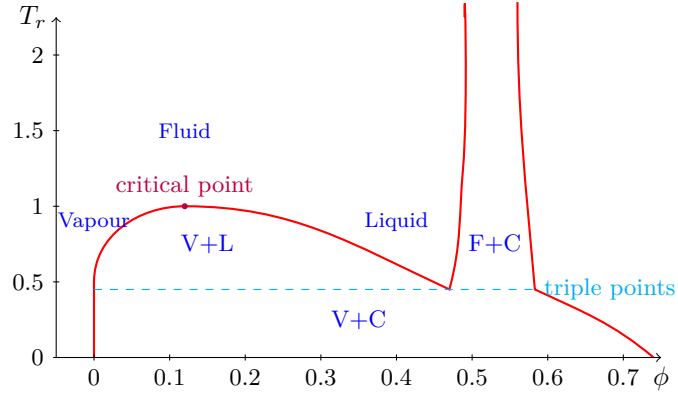


Figure 3.7: Longuet–Higgins–Widom-style phase diagram for the ‘exact’ Van der Waals model. This phase diagram was computed by using the hard-sphere system as a reference system and adding a weak, long-ranged attractive interaction.

Appendices

A Thermodynamics

A.1 The First Law

Theorem A.1. Let $\mathring{d}q$ be the heat transferred to a system and let $\mathring{d}w$ be the work done to the system. Then the change in the energy of the system is given by

$$\Delta E = \mathring{d}q + \mathring{d}w . \tag{A.1}$$