Chapter 7

The Chemical Potential and Phase Equilibria

We discuss the nature of the chemical potential by considering some simple models and simulations. We then discuss the role of the chemical potential in understanding phase transitions with a focus on the van der Waals equation of state. We also discuss chemical reactions and the law of mass action.

7.1 Meaning of the chemical potential

Although the chemical potential plays a role analogous to that of temperature and pressure, understanding the nature of the chemical potential is more difficult. We know that, if two systems are at different temperatures and are then placed in thermal contact, there will be a net transfer of energy from one system to the other until the temperatures of the two systems become equal. If there is a movable wall between two systems at different pressures, then the wall will move so as to change the volume of each system to make the pressures equal. Similarly, if two systems are initially at different chemical potentials and are then allowed to exchange particles, there will be a net transfer of particles from the system at the higher chemical potential to the one at the lower chemical potential until the chemical potentials become equal. You are asked to derive this result in Problem 1.1.

Problem 7.1. Chemical equilibrium

Assume that two systems A and B are initially in thermal and mechanical equilibrium, but not in chemical equilibrium, that is, $T_A = T_B$, $P_A = P_B$, but $\mu_A \neq \mu_B$. Use reasoning similar to that used in Section 2.13 to show that particles will be transferred from the system at the higher chemical potential to the system at the lower chemical potential. An easy way to remember the

N_A	$\Omega_A(N_A)$	$\ln \Omega_A(N_A)$	μ_A/kT	N_B	$\Omega_B(N_B)$	$\ln \Omega_B(N_B)$	μ_B/kT	$\Omega_A\Omega_B$
1	1	0	$-$	9	1287	7.16	$-$	1287
2	9	2.20	-1.90	8	792	6.68	-0.51	7128
3	45	3.81	-1.45	7	462	6.14	-0.57	20790
4	165	5.11	-1.20	6	252	5.53	-0.65	41580
5	495	6.21	-1.03	5	126	4.84	-0.75	62370
6	1287	7.16	$\mathbf{-0.90}$	4	56	4.03	$\mathbf{-0.90}$	72072
7	3003	8.01	-0.81	3	21	3.05	-1.12	63063
8	6435	8.77	-0.73	2	6	1.79	-1.52	38610
9	12870	9.46	$-$	1	1	0	$-$	12870

Table 7.1: The number of states of subsystems A and B such that the composite Einstein solid has a total number of particles $N = N_A + N_B = 10$ with $E_A = 8$ and $E_B = 5$. The number of microstates of each macrostate is determined using (4.3). Neither N_A nor N_B can equal zero, because each subsystem has a nonzero energy and thus each subsystem must have at least one particle. The quantity μ/kT in columns 4 and 8 is determined by computing the ratio $-\Delta \ln \Omega/\Delta N$, with $\Delta N = 1$. The most probable macrostate corresponds to $\tilde{N}_A \approx 6$. The ratio μ/kT is the same (to two decimal places) for both subsystems for this macrostate. The fraction of microstates associated with the most probable macrostate is $72072/319770 \approx 0.23$, where 319770 is the total number of microstates. This fraction will approach 1 as the number of particles and the total energy in the two subsystems become very large.

various thermodynamic relations for μ is to start from the fundamental thermodynamic relation in the form $dE = TdS - PdV + \mu dN$. □

To gain more insight into the nature of the chemical potential we discuss two models for which we can calculate the chemical potential explicitly, the Einstein solid and an ideal gas. In Chapter 4 we considered an Einstein solid consisting of two subsystems each with a fixed number of particles, but with different energies such that the total energy was fixed. We found that the temperatures of the two subsystems are equal for the energy distribution that has the largest number of microstates, and thus is most probable.

We now consider a similar composite Einstein solid consisting of two subsystems each with a variable number of particles such that the total number of particles is fixed, $N = N_A + N_B$. The energies E_A and E_B are fixed in each subsystem. In our example we take $N = N_A + N_B = 10$, $E_A = 8$, and $E_B = 5$. Table 1.1 displays the number of microstates in each subsystem and the total number of microstates in the composite system for the possible values of N_A and N_B. We see that the derivative of $\ln \Omega$ with respect to the number of particles in each subsystem, which equals $-\mu/kT$ [see (2.120), page 72], is almost equal (in our example the derivatives are equal to two decimal places) when the total number of microstates in the composite system is a maximum. We conclude that the quantity that becomes equal in equilibrium for this example is the ratio μ/T. In a more realistic example it would be impossible for particles to move from one system to another without transferring energy as well. In these systems both the temperature and chemical potential would individually become equal at equilibrium.

For the various composite Einstein solids that we considered in Chapter 4 we found that thermal equilibrium is achieved by energy being transferred from the hotter to the cooler subsystem.
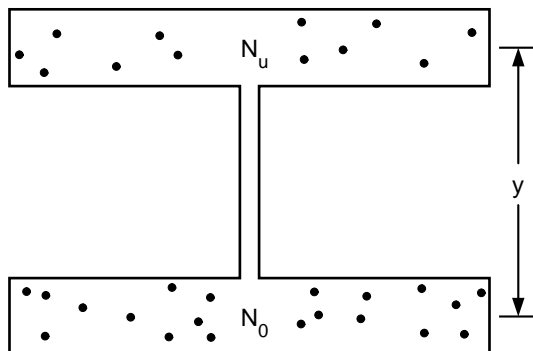
Figure 7.1: A container at height y connected by a tube of negligible volume to a container at height zero.

In the present example chemical equilibrium is reached by a transfer of particles. From Table 1.1 we see that if the two subsystems are initially not in equilibrium, for example, $N_A = 3$, then μ_A/T_A is less (more negative) than μ_B/T_B. Because the system will change to maximize the total entropy, we see that subsystem A will gain particles from subsystem B. Thus, particles will be transfered from a subsystem with the larger (less negative) ratio μ/T to the subsystem with the smaller value of μ/T.

Problem 7.2. Numerical calculation of the chemical potential of the Einstein solid

(a) Use Program `EinsteinSolidChemicalPotential` to consider an isolated Einstein solid consisting of two subsystems. The program counts the number of states using the relation (4.3). The inputs to the program are E_A, E_B, and $N = N_A + N_B$. Imagine that the two subsystems are initially separated by an insulating and impermeable partition, with $N_A = 8$, $N_B = 4$, $E_A = 15$, and $E_B = 30$. What is the initial entropy of the system? The partition is then replaced by one that allows particles but not energy to be transferred between the two subsystems. Construct a table similar to Table 1.1 and show that the ratio μ/T is approximately equal for the most probable macrostate (defined by specific values of N_A and N_B). Is the entropy of this macrostate higher than the initial entropy? Then try other combinations of N, E_A, and E_B. In a more realistic problem particles could not move from one system to another without transferring energy as well.

(b) Why is μ expected to be negative for the Einstein solid?

(c) If the amount of energy is the same in each subsystem of a composite Einstein solid, what would be the equilibrium number of particles in each subsystem? □

   We next consider a model consisting of two ideal gases that are in containers at different heights (see Figure 1.1).[1] Because we wish to characterize the containers only by their height, we assume that each container has a very large cross-sectional area and a very small thickness such that the volume of each container is finite. For simplicity, we also assume that both gases are at

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[1]This model is discussed in Baierlein [2001].

the same temperature T and volume V. The energy ϵ_i of the ith particle in either container is given by $\epsilon_i = mv_i^2/2 + mgy_i$, where m is its mass, v_i its speed, and y_i its height, which is either 0 or y. The acceleration due to the gravitational field is denoted by the constant g. We use the subscripts 0 and u to denote the lower and upper container, respectively.

The partition function for each container is a function of its volume, temperature, number of particles, and height. From (6.25) $Z_0(T, V, N_0)$ is given by [see (6.25), page 297]

$$Z_0(T, V, N_0) = \frac{V^{N_0}}{N_0!}\Big(\frac{2\pi mkT}{h^2}\Big)^{3N_0/2}, \tag{7.1}$$

where N_0 is the number of particles in the lower container. Similarly, the partition function Z_u for the upper container can be written as

$$Z_u(T, V, N_u) = \frac{V^{N_u}}{N_u!}\Big(\frac{2\pi mkT}{h^2}\Big)^{3N_u/2} e^{-mgyN_u/kT}, \tag{7.2}$$

where N_u is the number of particles in the upper container. Note the factor of $e^{-mgyN_u/kT}$ in (1.2).

Problem 7.3. Derive the relation (1.2). □

To find the corresponding chemical potentials we use the relations $F = -kT \ln Z$ and $\mu = (\partial F/\partial N)_{T,V}$. Hence the chemical potential μ_0 for the lower container is [see (6.29)]

$$\mu_0 = -kT \ln\Big[\frac{V}{N_0}\Big(\frac{2\pi mkT}{h^2}\Big)^{3/2}\Big], \tag{7.3}$$

and the chemical potential for the upper container is given by

$$\mu_u = mgy - kT \ln\Big[\frac{V}{N_u}\Big(\frac{2\pi mkT}{h^2}\Big)^{3/2}\Big]. \tag{7.4}$$

If the two containers have the same number of particles, then the top container has the higher chemical potential as can be seen by comparing (1.3) and (1.4). What will happen if the two containers are connected by a tube of negligible volume so that particles may move from one system to the other? In this case the only quantities that may vary are the number of particles in each container. (We have assumed that they have the same temperature and volume.) Because the number of particles of the composite system $N = N_0 + N_u$ is fixed, there is only one independent variable, which we take to be N_0. This number will change to make the free energy of the composite system a minimum.

To find the total free energy we note that the partition function of the composite system is the product of the partition function for each container because there is no interaction between the particles in the two containers. Hence, we have

$$Z(T, V, N_0) = Z_0(T, V, N_0)Z_u(T, V, N_u). \tag{7.5}$$

We first calculate the total free energy $F = -kT \ln Z$, take the derivative of F with respect to N_0, and set the derivative equal to zero to find the condition for the minimum free energy. The total free energy is [see (6.26), page 297]

$$F = -kTN_0\Big[\ln\frac{V}{N_0} + \frac{3}{2}\ln\Big(\frac{2\pi mkT}{h^2}\Big) + 1\Big] - kTN_u\Big[\ln\frac{V}{N_u} + \frac{3}{2}\ln\Big(\frac{2\pi mkT}{h^2}\Big) + 1 - \frac{mgy}{kT}\Big]. \tag{7.6}$$

We substitute $N_u = N - N_0$, take the derivative of F with respect to N_0, and set the result equal to zero. The result is

$$N_u = N_0 e^{-mgy/kT}. \tag{7.7}$$

The same result would be obtained if we had expressed F in terms of N_u and found $\partial F/\partial N_u$.

Equation (1.7) relates the number of particles in each container at equilibrium and implies that $N_u < N_0$. Thus, if there is initially the same number of particles in each container, particles will be transferred from the higher container to the lower one, that is, from the container at the higher chemical potential to the one at the lower chemical potential.

Problem 7.4. The chemical potential of a simple composite system

(a) Fill in the missing steps and derive (1.7).

(b) Show that $\mu_0 = \mu_u$ when the condition (1.7) is satisfied. Thus the chemical potentials of each part of the composite system are equal at equilibrium. ☐

Equation (1.7) tells us how the number density varies with height assuming that the temperature is independent of height, which is only approximately valid in our atmosphere. (This result was first obtained in Problem 6.48.) We can use similar considerations to show that, if two fluids are separated by a membrane with an electrical potential energy difference $q\Delta V$ between them, then the chemical potential difference between the two fluids will contain a term equal to $q\Delta V$. Here q is the magnitude of the charge of an ion in the fluid and ΔV is the potential difference. The transfer of ions across a cell membrane is due to the creation of a potential difference that produces a difference in the chemical potentials and causes ions to be transferred from a region of higher chemical potential to a region of lower chemical potential.

7.2 Measuring the chemical potential in simulations

7.2.1 The Widom insertion method

Another way of gaining more insight into the meaning of the chemical potential is to think about how we would measure it on a computer. From (2.151) and (4.102) we can write the chemical potential as

$$\mu = \left(\frac{\partial F}{\partial N}\right)_{T,V} \approx F_{N+1} - F_N = -kT \ln \frac{Z_{N+1}}{Z_N} \qquad (N \gg 1). \tag{7.8}$$

That is, the chemical potential is the change in the free energy of a system due to the addition of a particle (in the thermodynamic limit). To understand how we can estimate the chemical potential by a Monte Carlo simulation in the canonical ensemble we need to write μ in terms of the appropriate average. The partition function of a N particle system is $Z_N = \sum_s e^{-\beta E_s}$, where E_s is the energy of microstate s with N particles. Similarly, $Z_{N+1} = \sum_{s,r} e^{-\beta E_{s,r}}$, where the sum over r is over all possible coordinates and momenta of the additional particle, and $E_{s,r}$ is the energy when N particles are in the state s, and the additional particle is in state r. We define the quantity $\Delta E_{s,r} \equiv E_{s,r} - E_s$, and rewrite (1.8) as

$$\frac{Z_{N+1}}{Z_N} = \frac{\sum_{s,r} e^{-\beta \Delta E_{s,r}} e^{-\beta E_s}}{\sum_s e^{-\beta E_s}}. \tag{7.9}$$

If we combine (1.8) and (1.9), we find

$$\mu = -kT \ln \left\langle \sum_r e^{-\beta \Delta E_{s,r}} \right\rangle, \tag{7.10}$$

where the average is over all N-particle states weighted by the N-particle Boltzmann factor $e^{-\beta E_s} / \sum_s e^{-\beta E_s}$.

For an ideal classical gas there is no interaction between the particles and thus $\Delta E_{s,r}$ does not depend on microstate s. Therefore the sum over s in the numerator of (1.9) cancels the sum over s in the denominator. The sum over r becomes an integral over the position and momentum of the added particle. The integral over the position equals the volume, and hence (1.10) reduces to

$$\mu_{\text{ideal}} = -kT \ln \left[\frac{V}{N} \int e^{-\beta p^2 / 2m} \frac{d^3 p}{h^3} \right]. \tag{7.11}$$

The factor of $1/N$ accounts for the indistinguishability of the particles. Recall that $Z_N \propto 1/N!$ and thus $Z_{N+1}/Z_N \propto N!/(N+1)! = 1/(N+1) \approx 1/N$.

Problem 7.5. Chemical potential of an ideal classical gas

Show that (1.11) leads to the usual ideal classical gas expression for μ given in (6.29). ☐

The energy of the added particle consists of a kinetic energy term and a potential energy term. Because the integral over the momentum degrees of freedom is independent of the interparticle potential for a classical system of particles, a Monte Carlo simulation of a system need consider only the position coordinates. Hence, we need to determine only the change in the potential energy due to an added particle. It is common to write the chemical potential as $\mu = \mu_{\text{ideal}} + \mu_{\text{excess}}$, where μ_{ideal} is given in (1.11). From (1.10) we see that the "excess" contribution to the chemical potential can be expressed as

$$\mu_{\text{excess}} = -kT \ln \langle e^{-\beta \Delta U} \rangle, \tag{7.12}$$

where ΔU is the change in the potential energy when an imaginary test particle (of the same type) is added at random to a N-particle system.

Equation (1.12) can be used to estimate the chemical potential of gases and liquids. In a standard (Metropolis) Monte Carlo simulation of a system at a given temperature, the microstates of an N particle system are sampled in the usual way with the desired Boltzmann probability. Then a test particle is added periodically at a random position, the quantity $e^{-\beta \Delta U}$ is accumulated, and the particle is removed. The average in (1.12) is the accumulated sum of $e^{-\beta \Delta U}$ divided by the number of times a test particle was added. The addition of the test particle is virtual and it is not actually added.[2] This way of estimating μ is called the *Widom insertion method*.

We can use (1.12) to understand the density dependence of the chemical potential of a fluid. Consider a fluid for which the interaction between particles consists of a strongly repulsive potential at small particle separations and a weakly attractive potential that vanishes at large particle separations. At low densities the test particle will likely land in a region where the interparticle potential is small and negative, and thus the potential energy change due to the added particle

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[2]In principle, the sum over r in (1.10) should be done by adding many test particles in succession at random positions for a given microstate s. Because we sample such a small fraction of all the N-particle microstates, it is sufficient to periodically add only one particle to any particular N-particle microstate generated in the simulation.

will be small and negative ($\Delta U < 0$). In this case the exponential in (1.12) will be greater than 1, and thus the excess chemical potential will be negative. For higher densities an added particle is more likely to land near the potential minimum, and thus ΔU is likely to be more negative. Thus the excess chemical potential will initially decrease as the density is increased. For still higher densities the test particle will likely land on the steeply rising positive part of the potential, and thus ΔU will be large and positive, leading to $-\beta \Delta U < 0$, an exponential less than 1, and thus a positive excess chemical potential. We conclude that there is a minimum in the excess chemical potential as a function of density.

Problem 7.6. The excess chemical potential of a Lennard-Jones fluid

Program `WidomInsertionMethod` implements the Widom insertion method to estimate the chemical potential for a system of particles interacting with the Lennard-Jones potential. Determine the density dependence of the excess chemical potential of a Lennard-Jones fluid. Are your results for μ_{excess} consistent with our qualitative arguments? □

7.2.2 The chemical demon algorithm

In Sections 1.5 and 4.9 we discussed the demon algorithm and learned that the demon yields a measure of the temperature and that the temperature controls the transfer of energy between two systems. We now generalize the demon algorithm so that the demon carries two sacks, one for energy and one for particles. We will find that the generalized or chemical demon algorithm gives a measure of the chemical potential as well as the temperature, and that the chemical potential controls the transfer of particles between two systems.

We learned in Chapter 4 that, if the demon only exchanges energy with a system, then the probability that the demon has energy E_d is given by the Boltzmann distribution. If the demon can exchange both energy and particles with the system, then the probability $P(E_d, N_d)$ that the demon has energy E_d and N_d particles is given by the Gibbs distribution [see (4.142), page 217]:

$$P(E_d, N_d) = \frac{1}{Z_G} e^{-\beta(E_d - \mu N_d)}, \tag{7.13}$$

where Z_G is the grand canonical partition function. We can think of the demon as a system that exchanges energy and particles with a reservoir at constant T and μ.

To illustrate the nature of the chemical demon, we consider a one-dimensional system of particles. The position and momentum variables of the system are placed in bins of widths Δx and Δp, respectively, so that the phase space of the system is a two-dimensional lattice, with position in one direction and momentum in the other. The chemical demon algorithm can be summarized as follows:

1. Begin with an arbitrary initial configuration of the system with the desired total energy and total number of particles. The N particles of the system are randomly placed on the phase space lattice with no more than one particle on a lattice site. We set $E_d = 0$ and $N_d = 0$ for convenience, where E_d is the energy of the demon and N_d is the number of particles held by the demon.

2. Choose a lattice site (in phase space) at random. If there is a particle there, compute the trial change in energy ΔE that would result if the particle were removed.

3. If $\Delta E < E_d$, accept the move and subtract ΔE from E_d and let $N_d \to N_d + 1$. Otherwise reject the move, but include the unchanged configuration as the new configuration. Go to step 5.

4. If there is no particle at the lattice site and the demon has at least one particle, compute the trial change in energy ΔE needed to add a particle. If $\Delta E < E_d$, accept the addition and subtract ΔE from E_d and let $N_d \to N_d - 1$. Otherwise, retain the unchanged configuration.

5. Repeat steps 2–4 and allow the system to equilibrate before computing averages. Accumulate data for $P(E_d, N_d)$ after each MC step per lattice site.

Note that in this algorithm there is at most one particle at a given lattice site in phase space.

Program `ChemicalDemon` implements this algorithm and computes $P(E_d, N_d)$, the probability that the demon has energy E_d and N_d particles. From (1.13) we see that the slope of $P(E_d, N_d)$ versus E_d for fixed N_d is $-\beta$ and the slope of $P(E_d, N_d)$ versus N_d for fixed E_d is $\beta\mu$.

To see how the chemical demon algorithm can help us to understand the chemical potential, we first consider how the usual demon algorithm with only energy exchanges helps us understand the role of the temperature. Suppose that the demon is able to transfer energy into and out of the system very easily; that is, most of its trial changes are accepted. Under what conditions would the acceptance probability be close to 1? What can we say about the slope of $\ln P(E_d)$ versus E_d? The answer is that the slope would be shallow (and negative) because many demon energies would have nearly the same probability. We can also say that the temperature is high because the demon almost always has sufficient energy to give to the system when necessary. If instead the temperature is low, then a similar argument leads us to expect a steep negative slope for $\ln P(E_d)$ versus E_d. This behavior is independent of the size of the system because the exchange of energy affects only a small part of the system. This independence on the size of system explains why temperature is an intensive quantity.

Now consider the chemical demon and assume that it transfers particles only. From (1.13) we see that the ratio $-\mu/kT$ plays the analogous role for particle transfers as $1/kT$ does for energy. Because $-\mu/kT$ depends on both μ and T, it is more subtle to understand how the chemical potential behaves independently of the temperature. For this reason we assume in the following that the demon has already made a sufficient number of energy transfers so that the demon and the system are in thermal equilibrium.

For simplicity, consider a one-dimensional ideal gas, and let's see what we can infer by thinking about the demon's particle exchanges with the system. We know that the chemical potential is negative, which means that the slope of $\ln P(N_d)$ versus N_d is negative, and the probability of the demon having N_d particles decreases as N_d increases (for a given value of E_d). To understand this behavior consider the occupancy of the sites in two-dimensional phase space. Because the total energy E is fixed, particles will occupy sites with momentum in the range $\pm\sqrt{2mE}$. If the system is dilute, then there will be many empty cells in phase space with near zero momentum. If a particle from one of the higher momentum states is removed by the demon, it will give the demon lots of energy which can be used to return particles to the system at lower momentum sites. It will then be very difficult for the demon to add a particle to a high momentum state. Thus, the probability of the demon having N_d particles will decrease with N_d and the chemical potential must be negative. This argument illustrates how entropy arguments (which depend on the vast number of cells or sites in phase space) are essential for understanding the demon probabilities.

Problem 7.7. The chemical potential of a one-dimensional ideal gas

Program `ChemicalDemon` implements the chemical demon algorithm in which a demon exchanges particles (and energy) with a system of interest.

(a) Assume that the chemical demon exchanges energy and particles with a one-dimensional ideal classical gas. Choose the default parameters $N = 100$, $E = 200$, and $L = 100$, where N is the number of particles, E is the total energy of the system, and L is the length of the box. We use units such that the area of a cell in phase space is $\Delta x \Delta p = 1$. We also choose units such that $m = 1/2$ so that the energy of a particle is given by $\epsilon = p^2$. These choices imply that the momentum and energy are integers. The maximum momentum of a particle is $p_{\max} = \sqrt{E}$. The N particles are initially randomly placed in the cells of the phase space lattice with no more than one particle in a cell such that the desired total energy is obtained. For convenience we set the initial demon energy $E_d = 0$ and particle number $N_d = 0$. Run the simulation and discuss the qualitative features of the positions of the particles in phase space. Where are most of the particles located? Are there particles that have the same position? Run the simulation for different values of E, but the same values for the other parameters. Describe what you see in the phase space plots. Where in phase space are most of the particles located?

(b) Explain why the simulation in part (a) is identical to a simulation of an ideal gas in the semiclassical limit. Show that the chemical potential is given by

$$\mu = -T \ln[(L/N)(\pi T)^{1/2}]. \tag{7.14}$$

(Remember that our choice of units is equivalent to $\Delta x \Delta p = 1$.)

(c) Use the same parameters as in part (a) and run for about 200 Monte Carlo steps per particle (mcs) for equilibration. Then click `Zero Averages` and average over at least 1000 mcs. (You can speed up the simulation by increasing the steps per display to 10 or 100.) After the simulation is stopped, click the `Calculate` button to compute the demon energy and particle number distributions. The plot of $\ln P(E_d, N_d = 1)$ versus E_d should be approximately linear for small E_d. The inverse slope is related to the temperature. The plot of $\ln P(E_d = 1, N_d)$ versus N_d should give a slope equal to μ/T. Compare your Monte Carlo results with the exact result that you found in part (b). ☐

*__Problem 7.8.__ The effects of interparticle interactions

Consider the effects of including interactions between the particles in a dilute classical gas. If the interaction has a hard core, no two particles can have the same position. This interaction makes it more difficult for the demon to return particles to the system, and we expect the chemical potential to be greater (less negative) than the noninteracting system at the same density.

(a) Use Program `ChemicalDemon` and confirm the effect of including a hard core on the chemical potential of the system.

(b) If we include an attractive interaction between particles that are nearest neighbors in position, the energy of the system will be lowered for some particle additions, thus giving the demon more energy and making it easier for the demon to find places in phase space to add particles. The result is a lowering of the chemical potential compared to the hard core system. Show that this trend is observed in your simulations. ☐
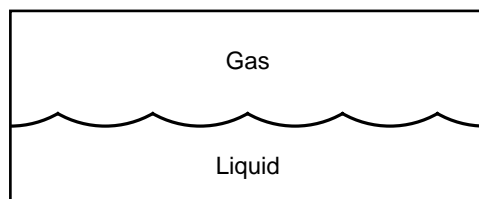
Figure 7.2: Gas-liquid phase separation in the presence of gravity. What would you observe in the absence of gravity? The two phases are in a closed container.

Our discussion suggests that the relative ease of the demon to exchange particles with a system is a measure of the system's chemical potential. We have previously concluded that the temperature is a measure of a system's ability to transfer energy. The chemical potential has an analogous role for the transfer of particles.

7.3   Phase Equilibria

Our considerations so far have been for homogeneous systems consisting of a single species. There are many circumstances for which a system separates into two homogeneous parts. The simplest example is of a closed container filled with the gas and liquid *phases* of the same substance (see Figure 1.2).

The particular phase chosen by a system depends on the pressure and temperature. For example, water is a liquid at room temperature and atmospheric pressure, but if it is cooled below $273.15\,\mathrm{K}$ at atmospheric pressure, it will eventually solidify and become ice. And if water is heated above $373.15\,\mathrm{K}$ it will vaporize.[3] At each of these temperatures, water undergoes dramatic changes in its properties, and we say that a *phase transition* occurs.

The existence of distinct phases is the result of intermolecular interactions, which are the same in all phases. The interaction of a water molecule, H_2O, with another water molecule is the same whether the molecule is in ice or in vapor. Why is the effect of the interactions so different macroscopically? The answer is the existence of *cooperative effects*, which we discussed briefly in Section 5.6.1 and will discuss in more detail in Chapters 8 and 9.

7.3.1   Equilibrium conditions

In some cases a system exists in only one phase, and in others two phases can coexist. For example, liquid water in equilibrium with its vapor inside a closed container is an example of two-phase coexistence. For simplicity, we will consider the conditions for equilibrium between two phases of a substance consisting of a single type of molecule.

We can understand the coexistence of phases by treating each phase as a subsystem. We know

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[3]If you were to place a thermometer in perfectly pure boiling water, the thermometer would very likely not read $100°$C. Superheating is almost inevitable. See Bohren and Albrecht [1998].

that for two systems A and B in thermal equilibrium, their temperatures must be equal:

$$T_A = T_B. \tag{7.15}$$

We also have shown that the pressure of the two phases must be equal in mechanical equilibrium,

$$P_A = P_B, \tag{7.16}$$

because the forces exerted by the two phases on each other at their surface of contact must be equal and opposite.

We will show in the following that, because the number of particles N_A and N_B in each phase can vary, the chemical potentials of the two phases must be equal:

$$\mu_A(T, P) = \mu_B(T, P). \tag{7.17}$$

We have written $\mu(T, P)$ because the temperature and pressure of the two phases are the same.

Because $\mu(T, P) = g(T, P)$ [see (2.156), page 78], where g is the Gibbs free energy per particle, we can also write the equilibrium condition (1.17) as

$$g_A(T, P) = g_B(T, P). \tag{7.18}$$

We now derive the equilibrium condition (1.17) or (1.18). Because T and P are well-defined quantities for a system of two phases, the natural thermodynamic potential is the Gibbs free energy G. Let N_i be the number of particles in phase i and $g_i(T, P)$ be the Gibbs free energy per particle in phase i. Then G can be written as

$$G = N_A g_A + N_B g_B. \tag{7.19}$$

The total number of particles is constant:

$$N = N_A + N_B = \text{constant}. \tag{7.20}$$

Suppose we let N_A vary. Because G is a minimum in equilibrium (for a given value of T and P), we have

$$dG = 0 = g_A dN_A + g_B dN_B = (g_A - g_B)dN_A, \tag{7.21}$$

where $dN_B = -dN_A$. Hence, we find that a necessary condition for equilibrium is $g_A(T, P) = g_B(T, P)$.

7.3.2 Simple phase diagrams

A typical phase diagram for a simple substance is shown in Figure 1.3(a). The lines represent the phase coexistence curves between the solid and liquid phases, the solid and vapor phases, and the liquid and vapor phases. The condition $g_A = g_B = g_C$ for the coexistence of all three phases leads to a unique temperature and pressure that defines the *triple point*. This unique property of the triple point makes the triple point of water a good choice for a readily reproducible temperature reference point. If we move along the liquid-gas coexistence curve toward higher temperatures, the two phases become more and more alike. At the *critical point*, the liquid-gas coexistence curve
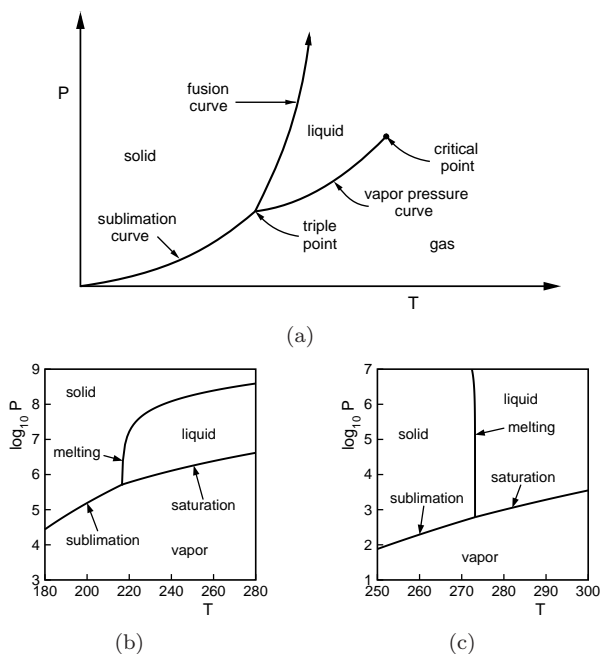
Figure 7.3: (a) Sketch of a typical phase diagram of a simple substance. The phase diagram shows the coexistence curves between the solid, liquid, and gas phases. All three phases coexist at the triple point. For temperatures and pressures above the critical point it is not possible to distinguish between a gas and a liquid, and the substance is known as a supercritical fluid. (b) Phase diagram of carbon dioxide with the pressure in pascals and the temperature in kelvin. The logarithm of the pressure is plotted so that the wide range of pressures can be shown. Note the positive slope of the melting curve with pressure. The triple point is at $T_{tp} = 216.6\,$K and $P_{tp} = 5.2 \times 10^5\,$Pa. Not shown is the critical point at $T_c = 304.1\,$K and $P_c = 7.38 \times 10^6\,$Pa. At atmospheric pressure and room temperature the solid and liquid phases are not stable, and dry ice (solid CO_2) will evaporate directly into a gas. (c) The phase diagram of water. Note the negative slope of the melting curve with pressure. For water $T_{tp} = 273.16\,$K, $P_{tp} = 611.66\,$Pa, $T_c = 647.31\,$K, and $P_c = 22.106 \times 10^6\,$Pa. The information for CO_2 and H_2O is from Glasser (2002, 2004).

ends, and there is no longer a distinction between a gas and a liquid. Note that a system can cross the phase boundary from its solid phase directly to its vapor without passing through the liquid phase, a transformation known as *sublimation*. An important commercial process that exploits this transformation is freeze drying.

The condition (1.17) [or (1.18)] for the coexistence of two phases implies that two phases cannot be in equilibrium with each other at all temperatures and pressures. If two phases of a substance coexist, only T or P can be chosen freely, but not both. For example, if liquid water is in equilibrium with its vapor, then the pressure of the water equals the vapor pressure, which is a unique function of the temperature. If the pressure is increased above the vapor pressure, the vapor will condense. If the pressure is decreased below the vapor pressure, the liquid will evaporate.

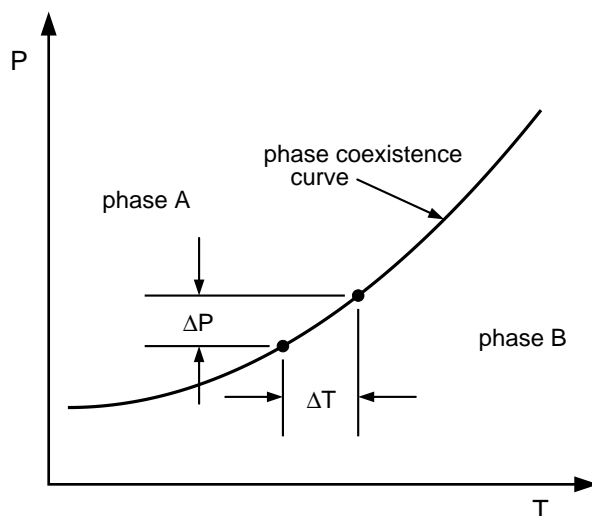Suppose that a fraction x of the particles is in phase A and a fraction $1 - x$ of the particles is

Figure 7.4: Derivation of the Clausius-Clapeyron equation.

in phase B. For values of T and P on the phase boundary where $g_A = g_B$, the Gibbs free energy is equal to $G = xNg_A + (1 - x)Ng_B = Ng_A = Ng_B$, which is independent of x. Hence for values of P and T on the phase boundary, the two phases can coexist in equilibrium in any proportion. The locus of points (T, P) such that $g_A = g_B$ is called the *phase coexistence curve*.

The quantity g_i is a well-defined function that is characteristic of the particular phase i. If T and P are such that $g_A < g_B$, then the minimum value of G corresponds to all N particles in phase A, $G = Ng_A$, and this phase is said to be *stable*. If T and P are such that $g_A > g_B$, then the minimum value of G corresponds to all N particles in phase B so that $G = Ng_B$. If, for example, the values of T and P correspond to the stable phase being a gas, then a rapid quench of the temperature to a value such that the liquid phase becomes stable, might lead to the gas phase becoming *metastable*. In this case we say that the gas is *supercooled*. The system will remain in the gas phase for some time until spontaneous density fluctuations drive the system to the stable liquid phase.

7.3.3   Clausius-Clapeyron equation

We now show that the equilibrium condition (1.18) leads to an equation for the slope of the phase coexistence curve. Consider two points on the phase coexistence curve, for example, one point at T, P and a nearby point at $T + \Delta T$ and $P + \Delta P$ (see Figure 1.4). The equilibrium condition (1.18) implies that $g_A(T, P) = g_B(T, P)$ and $g_A(T + \Delta T, P + \Delta P) = g_B(T + \Delta T, P + \Delta P)$. If we write $g_i(T + \Delta T, P + \Delta P) = g_i(T, P) + \Delta g_i$, we have

$$\Delta g_A = \Delta g_B, \tag{7.22}$$

or using (2.154)

$$- s_A \Delta T + v_A \Delta P = -s_B \Delta T + v_B \Delta P, \tag{7.23}$$

where s_i is the entropy per particle and v_i is the volume per particle in phase i. From (1.23) we have

$$\frac{dP}{dT} = \frac{s_B - s_A}{v_B - v_A} = \frac{\Delta s}{\Delta v}. \tag{7.24}$$

Thus, the slope of the coexistence curve at any point on the curve is equal to the ratio of entropy difference to the volume difference as the curve is crossed at that point. For N particles we have $\Delta S = N\Delta s$ and $\Delta V = N\Delta v$, and hence we can express (1.24) as

$$\frac{dP}{dT} = \frac{\Delta S}{\Delta V}. \tag{7.25}$$

From the relation $(\partial E/\partial V)_T = T(\partial S/\partial V)_T - P$ in (2.196) we can write

$$T\frac{\partial S}{\partial V} = \frac{\partial E}{\partial V} + P. \tag{7.26}$$

At the phase coexistence curve for a given T and P we have

$$T\frac{S_B - S_A}{V_B - V_A} = \frac{E_B - E_A}{V_B - V_A} + P, \tag{7.27}$$

or

$$T(S_B - S_A) = (E_B - E_A) + P(V_B - V_A). \tag{7.28}$$

Because the enthalpy $H = E + PV$, it follows that

$$L \equiv T(S_B - S_A) = H_B - H_A. \tag{7.29}$$

Thus we can write (1.25) as

$$\boxed{\frac{dP}{dT} = \frac{L}{T(V_B - V_A)}} \qquad \text{(Clausius-Clapeyron equation)}. \tag{7.30}$$

The relation (1.30) is called the *Clausius-Clapeyron equation*. It relates the slope of the phase coexistence curve at the point T, P to the enthalpy change or *latent heat L*,[4] the temperature at the phase boundary, and difference in the volumes of the two phases.

It usually is convenient to work with specific values of L and V, which we denote as ℓ and v, and to write (1.30) as

$$\frac{dP}{dT} = \frac{\ell}{T(v_B - v_A)}. \tag{7.31}$$

The energy ℓ required to melt a given amount of a solid is the *enthalpy of fusion*.[5] The enthalpy of fusion is related to the difference in the enthalpies of the liquid and the solid phase and is given by

$$\ell_{\text{fusion}} = h_{\text{liquid}} - h_{\text{solid}} = T(s_{\text{liquid}} - s_{\text{solid}}), \tag{7.32}$$

---

[4]The term latent heat is a relic from the time when it was thought that there were two kinds of heat: sensible heat, the kind you can feel, and latent heat, the kind you cannot.

[5]The more common name is *latent heat of fusion*.

where T is the melting temperature at the given pressure. Similarly, the equilibrium of a gas and liquid leads to the enthalpy of vaporization

$$\ell_{\text{vaporization}} = h_{\text{gas}} - h_{\text{liquid}}. \tag{7.33}$$

The enthalpy of sublimation associated with the equilibrium of gas and solid is given by

$$\ell_{\text{sublimation}} = h_{\text{gas}} - h_{\text{solid}}. \tag{7.34}$$

For most substances the slope of the solid-liquid coexistence curve is positive. The Clausius-Clapeyron equation shows that this positive slope is due to the fact that most substances expand on melting and therefore have $\Delta V > 0$. Water is an important exception and contracts when it melts. Hence, for water the slope of the melting curve is negative [see Figure 1.3(c)].

Example 7.1. Pressure dependence of the melting temperature of ice

Solution. Consider the equilibrium between ice and water as an example of the pressure dependence of the melting temperature of ice. The enthalpy of fusion of water at 0°C is

$$\ell_{\text{fusion}} = 3.35 \times 10^5 \, \text{J/kg}. \tag{7.35}$$

The specific volumes in the solid and liquid phase are

$$v_{\text{solid}} = 1.09070 \times 10^{-3} \, \text{m}^3/\text{kg}, \tag{7.36a}$$

$$v_{\text{liquid}} = 1.00013 \times 10^{-3} \, \text{m}^3/\text{kg}, \tag{7.36b}$$

so $\Delta v = v_{\text{liquid}} - v_{\text{solid}} = -0.0906 \times 10^{-3} \, \text{m}^3/\text{kg}$. If we substitute these values of ℓ and Δv in (1.31), we find

$$\frac{dP}{dT} = -\frac{3.35 \times 10^5}{273.2 \times (9.06 \times 10^{-5})} = -1.35 \times 10^7 \, \text{Pa/K}. \tag{7.37}$$

From (1.37) we see that an increase in pressure of 1.35×10^7 Pa (133 atm) lowers the melting temperature of ice by 1°C. ◊

The lowering of the melting point of ice under pressure is responsible for the motion of glaciers. The deeper parts of a glacier melt under the weight of ice on top allowing the bottom of a glacier to flow. The bottom freezes again when the pressure decreases.

It is sometimes said that ice skaters are able to skate freely because the pressure of the ice skates lowers the melting point of the ice and allows ice skaters to skate on a thin film of water between the blade and the ice. As soon as the pressure is released, the water refreezes. From Example 1.1 we see that if the ice is at -1°C, then the pressure due to the skates must be 135 atm for bulk melting to occur. However, even for extremely narrow skates and a large person, the skates do not exert enough pressure to lead to the melting of ice. For example, assume that the contact area of the blades to be 10^{-4} m^2 and the mass of the skater to be 100 kg. Then the pressure is given by $P = F/A = mg/A \approx 10^7$ Pa ≈ 100 atm. Because the temperature is frequently less than 0°C during the winter, there must be a mechanism other than pressure-induced melting which is responsible for ice skating. And how do we explain the slide of a hockey puck, which has a large surface area and a small weight? The answer is the existence of surface melting; that is, there is a layer of liquid water on the surface of ice which exists independently of the pressure of an ice skate (see the references).

Example 7.2. Pressure dependence of the boiling point

Because the change in the volume Δv is always positive for the transformation of a liquid to a gas, an increase in the pressure on a liquid always increases the boiling temperature. For water the enthalpy of vaporization is

$$\ell_{\text{vaporization}} = 2.257 \times 10^6 \, \text{J/kg}. \tag{7.38}$$

The specific volumes in the liquid and gas phase at $T = 373.15\,\text{K}$ and $P = 1\,\text{atm}$ are

$$v_{\text{liquid}} = 1.043 \times 10^{-3} \, \text{m}^3/\text{kg}, \tag{7.39a}$$

$$v_{\text{gas}} = 1.673 \, \text{m}^3/\text{kg}. \tag{7.39b}$$

Hence from (1.31) we have

$$\frac{dP}{dT} = \frac{2.257 \times 10^6}{373.15 \times 1.672} = 3.62 \times 10^3 \, \text{Pa/K}. \tag{7.40}$$

$\diamond$

Example 7.3. Liquid-gas coexistence curve

The Clausius-Clapeyron equation for the vapor pressure curve can be approximated by neglecting the specific volume of the liquid in comparison to the gas, $\Delta v = v_{\text{gas}} - v_{\text{liquid}} \approx v_{\text{gas}}$. From (1.39) we see that for water at its normal boiling point, this approximation introduces an error of less than 0.1%. If we assume that the vapor behaves like an ideal gas, then $v_{\text{gas}} = RT/P$ for one mole of the gas. (The gas constant $R = kN_A$, where N_A is Avogadro's number.) With these approximations, (1.31) can be written as

$$\frac{dP}{P} = \ell \frac{dT}{RT^2}, \tag{7.41}$$

where ℓ is the enthalpy of vaporization of one mole. If we also assume that ℓ is approximately temperature independent, we can integrate (1.41) to find

$$\ln P(T) = -\frac{\ell}{RT} + \text{constant}, \tag{7.42}$$

or

$$P(T) \approx P_0 \, e^{-\ell/RT}, \tag{7.43}$$

where P_0 is a constant. $\diamond$

Example 7.4. Liquid-solid coexistence curve

To find an equation for the phase coexistence curve between the liquid and solid phases it is reasonable to assume that the temperature dependence of ℓ and Δv can be neglected. In this approximation we can write (1.31) as

$$dP = \frac{\ell}{\Delta v} \frac{dT}{T}, \tag{7.44}$$

which can be integrated to give

$$P = P_0 + \frac{\ell}{\Delta v} \ln \frac{T}{T_0}, \tag{7.45}$$

where T_0, P_0 is a point on the phase coexistence curve. Because the volume change Δv between the liquid and the solid is small and the entropy change is large, the slope of the coexistence curve in the P-T plane is very steep (see Figure 1.3). $\diamond$

Example 7.5. The triple point of ammonia

In the vicinity of the triple point the liquid-vapor coexistence curve of liquid ammonia is given by $\ln P = 24.38 - 3063/T$, where the pressure is given in pascals and the temperature is in kelvins. The vapor pressure of solid ammonia is $\ln P = 27.92 - 3754/T$. What are the temperature and pressure at the triple point? What are the enthalpies of sublimation and vaporization? What is the enthalpy of fusion at the triple point?

Solution. At the triple point, $P_{\text{solid}} = P_{\text{liquid}}$ or $24.38 - 3063/T = 27.92 - 3754/T$. The solution is $T = 691/3.54 = 195.2\,\text{K}$. The corresponding pressure is $e^{8.7} = 5934\,\text{Pa}$. The relation (1.42), $\ln P = -\ell/RT + \text{constant}$, can be used to find the enthalpy of sublimation and vaporization of ammonia at the triple point. We have $\ell_{\text{sublimation}} = 3754R = 3.12 \times 10^4\,\text{J/mol}$ and $\ell_{\text{vaporization}} = 3063R = 2.55 \times 10^4\,\text{J/mol}$. The enthalpy of melting satisfies the relation $\ell_{\text{sublimation}} = \ell_{\text{vaporization}} + \ell_{\text{fusion}}$. Hence, $\ell_{\text{fusion}} = (3.12 - 2.55) \times 10^4 = 5.74 \times 10^3\,\text{J/mol}$. $\Diamond$

7.4   The van der Waals Equation of State

7.4.1   Maxwell construction

To gain more insight into the liquid-gas coexistence curve, we explore some of the properties of the van der Waals equation of state, which we repeat here for convenience:

$$P = \frac{NkT}{V - Nb} - \frac{aN^2}{V^2} \tag{7.46}$$

$$= \frac{\rho kT}{1 - \rho b} - a\rho^2, \tag{7.47}$$

where the density $\rho = N/V$. It is convenient to rewrite (1.47) in terms of the dimensionless variables

$$\tilde{P} = 27\left(\frac{b^2}{a}\right)P, \tag{7.48}$$

$$\tilde{T} = \frac{27}{8}\left(\frac{b}{a}\right)kT, \tag{7.49}$$

$$\tilde{\rho} = 3b\rho. \tag{7.50}$$

The reason for the numerical factors will become clear in the following (see Problem 1.10). The van der Waals pressure equation of state (1.47) in terms of these dimensionless variables becomes

$$\tilde{P} = \frac{8\tilde{\rho}\tilde{T}}{3 - \tilde{\rho}} - 3\tilde{\rho}^2, \tag{7.51}$$

Note that the equation of state in terms of the dimensionless variables $\tilde{P}$, $\tilde{T}$, and $\tilde{\rho}$ does not depend explicitly on the material dependent parameters a and b.

Problem 7.9. Dimensionless form of the van der Waals equation of state

Use the definitions (1.48)–(1.50) of $\tilde{P}$, $\tilde{T}$, and $\tilde{\rho}$ to derive (1.51). $\square$
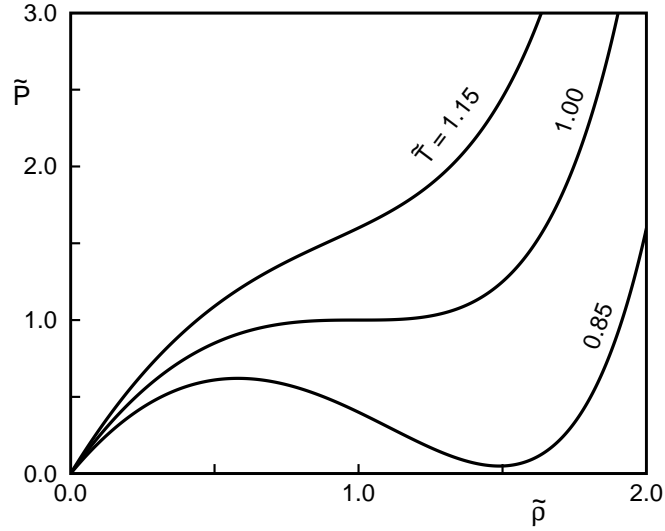
Figure 7.5: Three isotherms for a van der Waals fluid in terms of the dimensionless pressure $\tilde{P}$ and dimensionless density $\tilde{\rho}$ for the dimensionless temperatures $\tilde{T} = 1.15$, 1.0, and 0.85. Note that there is an inflection point at $\tilde{T} = 1$ and $\tilde{\rho} = 1$.

We plot $\tilde{P}$ versus $\tilde{\rho}$ for various temperatures in Figure 1.5. For high temperatures $\tilde{P}$ is a monotonically increasing function of $\tilde{\rho}$ as we would expect. For smaller $\tilde{T}$ there is an inflection point at $\tilde{T} = 1$ and $\tilde{\rho} = 1$. For values of $\tilde{T} \lesssim 1$ we see that $\tilde{P}$ has a local minimum for nonzero $\tilde{\rho}$. This behavior of the van der Waals equation of state is unphysical, and the pressure must be a monotonically increasing function of the density for all temperatures. In other words, a small expansion of the volume of the system should result in a decrease in the pressure. If the opposite happened, the pressure would increase and the volume would continue to increase.

We can make this requirement more precise by considering the isothermal compressibility κ, which is defined as [see (2.172)]

$$\kappa = -\frac{1}{V}\Big(\frac{\partial V}{\partial P}\Big)_{T,N} = \frac{1}{\rho}\Big(\frac{\partial \rho}{\partial P}\Big)_{T,N}. \tag{7.52}$$

Hence, the requirement that $\kappa > 0$ is equivalent to the condition that $(\partial P/\partial \rho)_{T,N} > 0$.[6] From Figure 1.5 we see that this inequality is satisfied for $\tilde{T} > \tilde{T}_c$, where $\tilde{T}_c$ is the temperature corresponding to the inflection point at which

$$\Big(\frac{\partial \tilde{P}}{\partial \tilde{\rho}}\Big)_{\tilde{T}_c,N} = 0, \tag{7.53}$$

$$\Big(\frac{\partial^2 \tilde{P}}{\partial \tilde{\rho}^2}\Big)_{\tilde{T}_c,N} = 0. \tag{7.54}$$

---

[6]The inequalities $\kappa > 0$ and $C_V > 0$ can be easily derived in the canonical ensemble [see (6.238) and (4.88)].

Problem 7.10. The critical point of the van der Waals equation of state

(a) Use (1.53) and (1.54) to show that the critical point of the van der Waals equation of state is given by

$$\tilde{P}_c = 1, \tag{7.55a}$$

$$\tilde{T}_c = 1, \tag{7.55b}$$

$$\tilde{\rho}_c = 1. \tag{7.55c}$$

Hence, we can write the dimensionless variables $\tilde{T}$, $\tilde{P}$, and $\tilde{V}$ as $\tilde{T} = T/T_c$, $\tilde{P} = P/P_c$, and $\tilde{V} = V/V_c$. We now see why the various numerical factors were included in the definitions (1.48)–(1.50) of $\tilde{P}$, $\tilde{T}$, and $\tilde{\rho}$.

(b) Show that

$$\frac{V_c}{N} = 3b, \tag{7.56a}$$

$$P_c = \frac{a}{27b^2}, \tag{7.56b}$$

$$kT_c = \frac{8a}{27b}. \tag{7.56c}$$

(c) At what temperature does the compressibility become negative for a given value of the density?

(d) What is the value of the compressibility ratio $P_c/\rho_c kT_c$ according to the van der Waals equation of state? This ratio is close to ≈ 0.29 in a wide variety of systems ranging from Ne to CH_4. $\square$

One of the features of the van der Waals equation of state is that it predicts the *law of corresponding states*, which states that the equations of state of all fluids are identical if they are expressed in terms of dimensionless variables relative to their value at the critical point. This prediction holds only approximately in reality, but it is exact for the van der Waals equation of state; that is, (1.51) is independent of the material parameters a and b.

How can we understand the different nature of the $\tilde{P}$-$\tilde{\rho}$ diagram curves above and below T_c? For temperatures $T > T_c$ there is a unique value of the density for each value of the pressure. Hence a substance at a particular temperature above T_c can pass from a gas to a liquid and vice versa without passing through a phase transition where there would be a large change in some thermodynamic property such as the compressibility.

What happens below T_c? From Figure 1.5 we see that for $\tilde{P} < \tilde{P}_c$, there are three possible values of the density and there is a range of densities for which the system is not thermodynamically stable, that is, $\kappa < 0$. This instability is due to the fact that the van der Waals equation of state for $T < T_c$ is not exact and is not a good approximation of the behavior of $\tilde{P}(\tilde{\rho})$ for a real physical system. We will show in the following that it is possible to interpret the van der Waals phase diagram so that it does give physically reasonable results. In particular, we will find that there is a range of densities for which phase separation occurs and gas and liquid coexist.
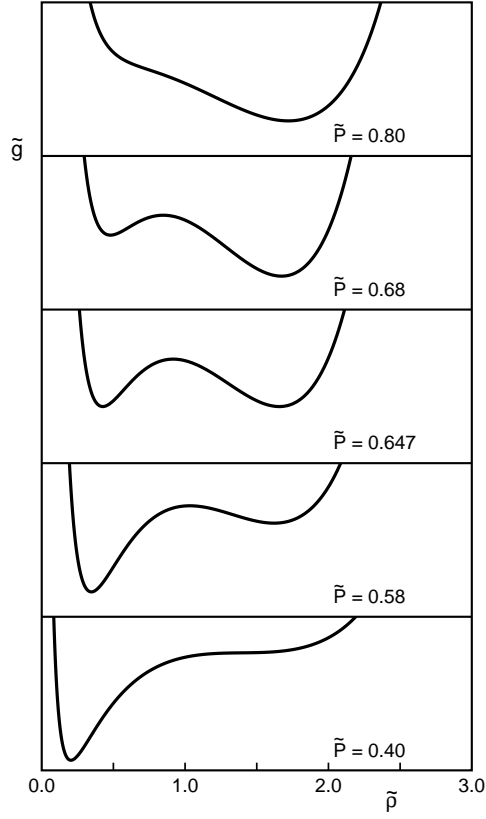
Figure 7.6: Plot of $\tilde{g}(\tilde{\rho})$ in (1.59) at $\tilde{T} = 0.9$ for (a) $\tilde{P} = 0.40$, (b) $\tilde{P} = 0.58$, (c) $\tilde{P} = 0.647$, (d) $\tilde{P} = 0.68$, and (e) $\tilde{P} = 0.80$. As $\tilde{P}$ is increased, the density that gives the minimum value of $\tilde{g}$ changes from the gas phase to the critical point where the two minima are equal, and then to the liquid phase at high density. The local minima correspond to metastable states.

To gain more insight into the nature of the van der Waals equation of state for $\tilde{T} < \tilde{T}_c$, we find the corresponding Gibbs free energy. To do so we first find the Helmholtz free energy F by integrating the relation $P = -(\partial F/\partial V)_T$, with P given by (1.46):

$$F = -NkT \ln(V - Nb) - \frac{aN^2}{V} + NkTw(T), \tag{7.57}$$

where $w(T)$ is an unknown function of T whose form is not needed in the following (see Problem 1.17). Hence, the Gibbs free energy is given by

$$G(T, P) = F + PV = -NkT \ln(V - Nb) - \frac{aN^2}{V} + PV + NkTw(T). \tag{7.58}$$

It is convenient to introduce the dimensionless Gibb's free energy per particle $\tilde{g} = 8G/3NkT_c$ and

rewrite (1.58) as

$$\tilde{g} = -3\tilde{\rho} - \frac{8}{3}\tilde{T}\ln\left(\frac{3}{\tilde{\rho}} - 1\right) + \tilde{P}/\tilde{\rho}, \tag{7.59}$$

where we have ignored terms that do not depend on $\tilde{\rho}$ or $\tilde{P}$.

The minimum of $\tilde{g}$ for a specific $\tilde{T}$ and $\tilde{P}$ determines the density at equilibrium. Plots of the Gibbs free energy per particle $\tilde{g}(\tilde{\rho})$ as a function of $\tilde{\rho}$ for different values of $\tilde{P}$ and fixed $\tilde{T} = 0.9$ are given in Figure 1.6. We see that for $\tilde{P} = 0.40$, $\tilde{g}$ has one minimum at $\tilde{\rho} \approx 0.20$ corresponding to the gas phase. At $\tilde{P} = 0.58$ there is a local minimum at $\tilde{\rho} \approx 1.66$ corresponding to the metastable liquid phase (a superheated liquid) and a global minimum at $\tilde{\rho} \approx 0.35$ corresponding to the stable gas phase. At $\tilde{P} = 0.647$ the two minima are equal corresponding to the coexistence of the liquid and gas phases. For $\tilde{P} = 0.68$ the global minimum at $\tilde{\rho} \approx 1.67$ corresponds to the liquid phase and the local minimum at $\tilde{\rho} \approx 0.48$ corresponds to the supercooled gas. Finally, for $\tilde{P} = 0.80$, there is only one minimum at $\tilde{\rho} \approx 1.72$, corresponding to the liquid phase.

Another way of understanding the behavior of the system for $\tilde{T} < \tilde{T}_c$ is given in Figure 1.7. Suppose that we prepare the system at the pressure $\tilde{P}_0 = 0.35$ corresponding to the stable gas phase. We then increase the pressure quasistatically, keeping $\tilde{T}$ fixed at $\tilde{T} = 0.9$. At $\tilde{P} \approx 0.42$, $\tilde{g}$ is multivalued, but because $\tilde{g}$ is a minimum for a given value of $\tilde{T}$ and $\tilde{P}$, the system will follow the lower curve until the point C where $\tilde{P} = 0.647$ and the two curves meet. At this value of the pressure the value of $\tilde{g}$ is the same for the gas and liquid phases, and the two phases coexist. As the pressure is increased further the system will follow the lower curve, and the system will be in the liquid phase. However, if we increase the pressure quickly, the system will likely follow the dashed curve and become a metastable gas until $\tilde{P} = 0.724$, the limit of metastability.[7] Similarly, if we start the system in the stable liquid phase and reduce the pressure quickly, the system is likely to follow the dashed curve corresponding to a metastable liquid. The system will remain in a metastable state until a spontaneous density fluctuation takes the system to the state of lower Gibbs free energy.

To find the pressure at which phase coexistence occurs at a given temperature we use the fact that $g(P_{\text{gas}}, T) = g(P_{\text{liq}}, T)$ and $P_{\text{gas}} = P_{\text{liq}} = P$ on the coexistence curve. Hence, we consider the difference $g(P_{\text{liq}}, T) - g(P_{\text{gas}}, T)$ and find the pressure P for a given value of T such that the difference is zero. We write

$$g(P_{\text{liq}}, T) - g(P_{\text{gas}}, T) = \int_{P_{\text{gas}}}^{P_{\text{liq}}} \left(\frac{\partial g}{\partial P}\right)_T dP = \int_{P_{\text{gas}}}^{P_{\text{liq}}} \frac{dP}{\rho}, \tag{7.60}$$

where we have used the Gibbs-Duhem equation (2.158) at constant temperature,

$$dg = d\mu = \frac{V}{N}dP = \frac{1}{\rho}dP. \tag{7.61}$$

---

[7]Above this pressure the system is thermodynamically unstable; that is, the compressibility becomes negative. The pressure at which the system becomes unstable (for a given temperature) is known as the *spinodal*. The spinodal is well defined only for mean-field equations of state such as the van der Waals equation.
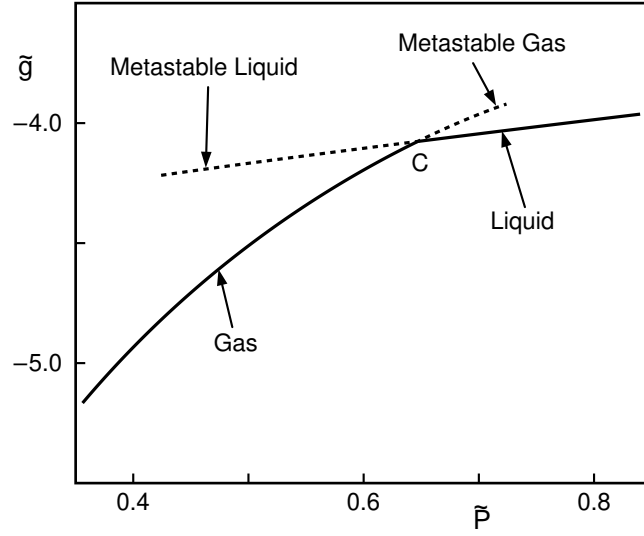
Figure 7.7: Plot of the dimensionless Gibbs free energy per particle $\tilde{g}$ as a function of $\tilde{P}$ at $T = 0.9T_c$ and fixed density. The system is metastable along the dashed curves.

We write the right-hand side of (1.60) as

$$\int_{P_{\text{gas}}}^{P_{\text{liq}}} \frac{dP}{\rho} = \int_{P_{\text{gas}}}^{P_{\text{liq}}} \left[d\left(\frac{P}{\rho}\right) - P d\left(\frac{1}{\rho}\right) \right] \tag{7.62a}$$

$$= \frac{P(\rho_{\text{liq}}, T)}{\rho_{\text{liq}}} - \frac{P(\rho_{\text{gas}}, T)}{\rho_{\text{gas}}} + \int_{\rho_{\text{gas}}}^{\rho_{\text{liq}}} \frac{P(\rho)}{\rho^2} d\rho. \tag{7.62b}$$

We substitute (1.62b) into (1.60) and obtain

$$g(\rho_{\text{liq}}, T) - g(\rho_{\text{gas}}, T) = \frac{P(\rho_{\text{liq}}, T)}{\rho_{\text{liq}}} - \frac{P(\rho_{\text{gas}}, T)}{\rho_{\text{gas}}} + \int_{\rho_{\text{gas}}}^{\rho_{\text{liq}}} \frac{P(\rho)}{\rho^2} d\rho. \tag{7.63}$$

Because $g(\rho_{\text{gas}}) = g(\rho_{\text{liq}})$ and $P(\rho_{\text{gas}}) = P(\rho_{\text{liq}}) = P$ on the phase coexistence curve, (1.63) reduces to

$$P\left[\frac{1}{\rho_{\text{liq}}} - \frac{1}{\rho_{\text{gas}}}\right] + \int_{\rho_{\text{gas}}}^{\rho_{\text{liq}}} \frac{P(\rho)}{\rho^2} d\rho = 0. \tag{7.64}$$

We can alternatively express (1.64) in terms of the volume per particle $v = 1/\rho$:

$$P\left[v_{\text{gas}} - v_{\text{liq}}\right] - \int_{v_{\text{liq}}}^{v_{\text{gas}}} P dv = 0. \tag{7.65}$$

The geometrical interpretation of (1.65) can be seen by looking at Figure 1.8. The values of P, v_{gas}, and v_{liq} are determined by choosing the shaded areas in Figure 1.8 to have equal areas. This way of interpreting the meaning of the van der Waals equation for $T < T_c$ is known as the
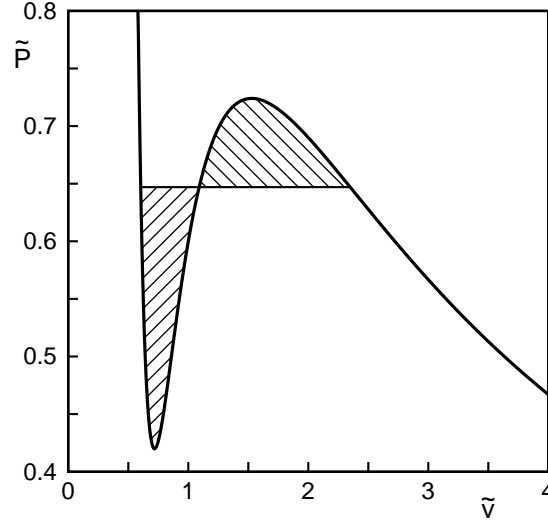
Figure 7.8: Maxwell equal area construction. The pressure $\tilde{P}$ where two phase coexistence begins for $\tilde{T} = 0.9$ is determined so that the areas above and below the horizontal line are equal. In this case $\tilde{P} \approx 0.647$.

Maxwell construction. This construction provides a recipe for finding the equilibrium values of P, v_{liq}, and v_{gas} along any isotherm at a temperature $T < T_c$.

   Liquid-gas coexistence curve for the van der Waals equation of state. We now use (1.65) to find the values of $\tilde{\rho}_{\mathrm{gas}}$ and $\tilde{\rho}_{\mathrm{liq}}$ for a given pressure $\tilde{P}$ and temperature $\tilde{T}$ on the coexistence curve. We write (1.51) on the coexistence curve:

$$\tilde{P} = \frac{8\tilde{\rho}_{\mathrm{gas}}\tilde{T}}{3 - \tilde{\rho}_{\mathrm{gas}}} - 3\tilde{\rho}_{\mathrm{gas}}^2 = \frac{8\tilde{\rho}_{\mathrm{liq}}\tilde{T}}{3 - \tilde{\rho}_{\mathrm{liq}}} - 3\tilde{\rho}_{\mathrm{liq}}^2, \tag{7.66}$$

and solve (1.66) for $\tilde{T} < \tilde{T}_c = 1$:

$$\tilde{T} = \frac{1}{8}(3 - \tilde{\rho}_{\mathrm{gas}})(3 - \tilde{\rho}_{\mathrm{liq}})(\tilde{\rho}_{\mathrm{gas}} + \tilde{\rho}_{\mathrm{liq}}). \tag{7.67}$$

We substitute $\tilde{T}$ from (1.67) into the right-hand side of (1.66) and find

$$\tilde{P} = \tilde{\rho}_{\mathrm{gas}}\tilde{\rho}_{\mathrm{liq}}\big[3 - \tilde{\rho}_{\mathrm{gas}} - \tilde{\rho}_{\mathrm{liq}}\big]. \tag{7.68}$$

We next substitute $\tilde{P}$ from (1.51) into the integral in (1.64) and evaluate the integral:

$$\int_{\tilde{\rho}_{\mathrm{gas}}}^{\tilde{\rho}_{\mathrm{liq}}} \frac{\tilde{P}(\tilde{\rho})}{\tilde{\rho}^2}\, d\tilde{\rho} = \int_{\tilde{\rho}_{\mathrm{gas}}}^{\tilde{\rho}_{\mathrm{liq}}} \frac{1}{\tilde{\rho}^2}\Big[\frac{8\tilde{\rho}\tilde{T}}{3 - \tilde{\rho}} - 3\tilde{\rho}^2\Big]\, d\tilde{\rho} \tag{7.69a}$$

$$= \Big[\frac{8\tilde{T}}{3}\ln\frac{\tilde{\rho}}{3 - \tilde{\rho}} - 3\tilde{\rho}\Big]_{\tilde{\rho}_{\mathrm{gas}}}^{\tilde{\rho}_{\mathrm{liq}}} \tag{7.69b}$$

$$= \frac{8\tilde{T}}{3}\ln\Big[\frac{\tilde{\rho}_{\mathrm{liq}}(3 - \tilde{\rho}_{\mathrm{gas}})}{\tilde{\rho}_{\mathrm{gas}}(3 - \tilde{\rho}_{\mathrm{liq}})}\Big] - 3(\tilde{\rho}_{\mathrm{liq}} - \tilde{\rho}_{\mathrm{gas}}). \tag{7.69c}$$
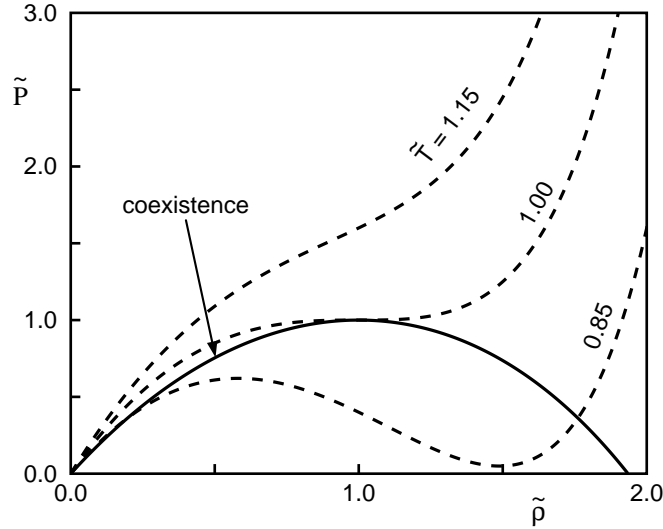
Figure 7.9: The coexistence curve for the van der Waals equation of state as a function of the dimensionless density $\tilde{\rho}$. Also plotted are three isotherms (dashed lines). For $\tilde{T} < 1$ the isotherms intersect the coexistence curve (solid line) at two points whose coordinates give the equilibrium values of $\tilde{P}$, $\tilde{\rho}_{\text{gas}}$, and $\tilde{\rho}_{\text{liq}}$. For $\tilde{T} = 1$ the isotherm intersects the coexistence curve at one point where $\tilde{P} = 1$ and $\tilde{\rho} = \tilde{\rho}_{\text{gas}} = \tilde{\rho}_{\text{liq}} = 1$.

Finally, we substitute $\tilde{P}$ from (1.68), $\tilde{T}$ from (1.67), and the integral in (1.69c) into (1.64) and obtain

$$(\tilde{\rho}_{\text{liq}} - \tilde{\rho}_{\text{gas}})(6 - \tilde{\rho}_{\text{gas}} - \tilde{\rho}_{\text{liq}}) = \frac{1}{3}(3 - \tilde{\rho}_{\text{gas}})(3 - \rho_{\text{liq}})(\tilde{\rho}_{\text{gas}} + \tilde{\rho}_{\text{liq}}) \ln \left[\frac{\tilde{\rho}_{\text{liq}}(3 - \tilde{\rho}_{\text{gas}})}{\tilde{\rho}_{\text{gas}}(3 - \tilde{\rho}_{\text{liq}})} \right]. \qquad (7.70)$$

The final result was obtained by multiplying both sides of the equation by -1, so that both sides are positive. We next use (1.67) for a particular value of $\tilde{T}$, compute $\tilde{\rho}_{\text{gas}}$ as a function of $\tilde{\rho}_{\text{liq}}$, and find $\tilde{\rho}_{\text{liq}}$ from a numerical solution of (1.70). We can then use this numerical solution in (1.67) to obtain the coexistence curve shown in Figure 1.9.

7.4.2   *The van der Waals critical point

We learned in Chapter 5 that the behavior of the Ising model near a critical point is characterized by power law behavior and critical exponents. In the following we will investigate the nature of the critical point as given by the van der Waals equation of state. We will see that the gas-liquid critical point shows similar behavior and is characterized by mean-field exponents. That is, the van der Waals equation of state is a mean-field equation.

We have already found the values of T_c, P_c, and ρ_c. Suppose that we fix the pressure and the density at their critical point values and lower the temperature starting from above T_c. Then the critical point is where the system must first choose between being a liquid or a gas.

Near the critical point we can write

$$\tilde{\rho}_{\text{liq}} = \tilde{\rho}_c + \Delta_{\text{liq}} = 1 + \Delta_{\text{liq}}, \tag{7.71a}$$

$$\tilde{\rho}_{\text{gas}} = \tilde{\rho}_c - \Delta_{\text{gas}} = 1 - \Delta_{\text{gas}}. \tag{7.71b}$$

We substitute (1.71) into (1.70) and expand each side in powers of Δ_{liq} and Δ_{gas}. To first order in Δ_{liq} and Δ_{gas} we find that $\Delta_{\text{liq}} = \Delta_{\text{gas}}$. That is, the coexistence curve is symmetrical near the critical point (see Problem 1.11). This symmetry is a special case of the empirical law of "rectilinear diameters," which is exact for the van der Waals equation of state and a good approximation for real systems.

Problem 7.11. Symmetry of the van der Waals coexistence line near the critical point

Consider the van der Waals equation along the coexistence line as given by (1.70). Use (1.71) and show that to leading order in Δ_{liq} and Δ_{gas} that the coexistence curve is symmetrical, that is, $\Delta_{\text{liq}} = \Delta_{\text{gas}}$. □

Next we find how the difference $\rho_{\text{liq}} - \rho_{\text{gas}}$ goes to zero as $T \to T_c$ along the coexistence curve. We subtract $\tilde{T}_c = 1$ from both sides of (1.67), expand the right-hand side in powers of Δ_{liq} and Δ_{gas}, and obtain

$$\tilde{T} - \tilde{T}_c = \frac{1}{8}(3 - \tilde{\rho}_{\text{gas}})(3 - \tilde{\rho}_{\text{liq}})(\tilde{\rho}_{\text{gas}} + \tilde{\rho}_{\text{liq}}) - 1 \tag{7.72a}$$

$$= \frac{1}{8}\left[(2 + \Delta_{\text{gas}})(2 - \Delta_{\text{liq}})(2 + \Delta_{\text{liq}} - \Delta_{\text{gas}})\right] - 1 \tag{7.72b}$$

$$\approx \frac{1}{4}\left[\Delta_{\text{gas}}\Delta_{\text{liq}} - \Delta_{\text{gas}}^2 - \Delta_{\text{liq}}^2\right]. \tag{7.72c}$$

We then let $\Delta_{\text{liq}} = \Delta_{\text{gas}} = \Delta$ and write (1.72c) as

$$\tilde{T} - \tilde{T}_c \approx -\frac{1}{4}\Delta^2 \tag{7.73}$$

or

$$\tilde{\rho}_{\text{liq}} - \tilde{\rho}_c = \tilde{\rho}_c - \tilde{\rho}_{\text{gas}} \sim \left(\tilde{T}_c - \tilde{T}\right)^{1/2}. \tag{7.74}$$

In our discussion of the critical point in the Ising model in Chapter 5, we found that the order parameter m vanishes near T_c from below as $m \propto (T_c - T)^\beta$, where $\beta = 1/2$ in mean-field theory. We can similarly choose the quantity $\tilde{\rho}_{\text{liq}} - \tilde{\rho}_c$ as the order parameter of the gas-liquid critical point. Hence, we see from (1.74) that the van der Waals theory predicts $\beta = 1/2$, a manifestation of the mean-field nature of the van der Waals theory.

Just as we considered the divergence of the susceptibility near the Ising critical point, we now consider the temperature dependence of the isothermal compressibility near the gas-liquid critical point. From the definition (1.52) and the van der Waals equation of state in (1.50) we have

$$\kappa = \frac{27b^2}{a}\frac{1}{\tilde{\rho}}\left(\frac{\partial \tilde{\rho}}{\partial \tilde{P}}\right)_{T,N}, \tag{7.75}$$

and

$$\frac{\partial \tilde{P}}{\partial \tilde{\rho}} = \frac{24\tilde{T}}{(3 - \tilde{\rho})^2} - 6\tilde{\rho}. \tag{7.76}$$

Note that if we set $\tilde{T} = \tilde{T}_c = 1$ and $\tilde{\rho} = \tilde{\rho}_c = 1$ in (1.76) we find $\partial \tilde{P}/\partial \tilde{\rho} = 0$, and we conclude that the compressibility diverges at the critical point. To see how κ behaves for $\tilde{T}$ near $\tilde{T}_c$ we let $\tilde{\rho} = 1 + \Delta$, and write

$$\frac{\partial \tilde{P}}{\partial \tilde{\rho}} = \frac{24\tilde{T}}{(2 - \Delta)^2} - 6(1 + \Delta) \approx \frac{3}{4}\Delta^2. \tag{7.77}$$

Hence κ at $\tilde{\rho} = \tilde{\rho}_c = 1$ diverges as

$$\kappa \approx \Delta^{-2} \propto (\tilde{T}_c - \tilde{T})^{-1}, \tag{7.78}$$

where the dependence on $(\tilde{T}_c - \tilde{T})$ is given in (1.74). Note that the (isothermal) compressibility κ and the (zero-field) magnetic susceptibility χ both diverge at the critical point with the exponent $\gamma = 1$, as predicted by the van der Waals equation of state and mean-field theory.

7.5   *Chemical Reactions

Consider a chemical reaction such as the production of water from hydrogen and oxygen,

$$2\text{H}_2 + \text{O}_2 \Leftrightarrow 2\text{H}_2\text{O}. \tag{7.79}$$
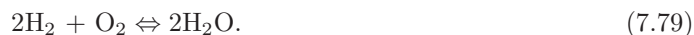
The symbol $\Leftrightarrow$ indicates that the reaction can go either way depending on the concentration of each molecular species and the temperature. Equation (1.79) says that it takes two molecules of hydrogen and one molecule of oxygen to make two molecules of water. We rewrite (1.79) in the standard form

$$- 2\text{H}_2 - \text{O}_2 + 2\text{H}_2\text{O} = 0, \tag{7.80}$$

or more generally

$$\nu_1 N_1 + \nu_2 N_2 + \nu_3 N_3 = 0, \tag{7.81}$$

where N_1 is the number of hydrogen molecules, N_2 is the number of oxygen molecules, and N_3 is the number of water molecules. The *stoichiometric* coefficients are $\nu_1 = -2$, $\nu_2 = -1$, and $\nu_3 = 2$. The (arbitrary) convention is that ν_i is positive for product molecules and negative for reactant molecules.

Imagine we place hydrogen, oxygen, and water in a closed container and allow them to react, perhaps by supplying a spark. Some of the hydrogen and oxygen will be converted to water, such that the number of hydrogen molecules is reduced and becomes twice that of oxygen, and the number of water molecules that is produced will be the same as the reduction of hydrogen molecules. Hence we can write

$$\nu_1 dN_1 + \nu_2 dN_2 + \nu_3 dN_3 = 0. \tag{7.82}$$

We can now determine the equilibrium conditions. We begin with the generalization of (2.154) to many kinds of molecules:

$$dG = -SdT + VdP + \sum_i \mu_i dN_i, \tag{7.83}$$

where μ_i is the chemical potential of molecules of type i. We know that the Gibbs free energy will be a minimum in equilibrium for a given pressure and temperature. The equilibrium condition $dG = 0$ yields (for given values of P and T)

$$0 = \sum_i \nu_i \mu_i. \tag{7.84}$$

The condition for chemical equilibrium for the reaction in (1.80) is

$$2\mu_{\mathrm{H_2}} + \mu_{\mathrm{O_2}} = 2\mu_{\mathrm{H_2O}}. \tag{7.85}$$

If the system is not in chemical equilibrium, then the sum on the right-hand side of (1.84) will not vanish. If the sum is negative, then the reaction proceeds spontaneously toward the products (the molecules on the right-hand side of the reaction equation); if it is positive, the reaction proceeds toward the reactants.

To find the relative concentrations of each type of molecule in equilibrium, we need to know how the chemical potential of each type of molecule depends on its concentration. For simplicity, we assume that the different molecules form a dilute gas which can be approximated as ideal. The reaction takes place in a closed container of volume V at temperature T. For such an idealized system thermodynamic quantities such as the mean energy and pressure are additive. For example, the total pressure is given by $\sum_i P_i$, where P_i is the pressure that would be exerted by the gas of type i if it was in the container all by itself. If we assume that the chemical potential of the ith type depends only on the number of molecules of that type and not on the number of molecules of other types in the container, then the chemical potential for molecules of type i is given by [see (6.115)]

$$\mu_i(T, V, N_i) = -kT \ln \left[\frac{V}{N_i} \left(\frac{2\pi m_i kT}{h^2} \right)^{3/2} \right] = -kT \ln \left[\frac{V}{N} \frac{N}{N_i} \left(\frac{2\pi m_i kT}{h^2} \right)^{3/2} \right]. \tag{7.86}$$

If we replace V/N by kT/P and let $n_i = N_i/N$, we can rewrite (1.86) as

$$\mu_i(T, P, n_i) = -kT \ln \left[\frac{kT}{P} \left(\frac{2\pi m_i kT}{h^2} \right)^{3/2} \right] + kT \ln n_i, \tag{7.87}$$

which we write as

$$\mu_i(T, P, n_i) = \mu_i^{(0)}(T, P) + kT \ln n_i, \tag{7.88}$$

where $\mu_i^{(0)}(T, P)$ is the chemical potential of a pure system consisting of molecules of type i at temperature T and pressure P. The assumption that the chemical potential of the ith type depends only on the fraction of the ith type present, and not on the fractions of the other types, does not hold in general. This assumption is applicable when the types of molecules that are mixed are chemically similar, in dilute solutions that do not involve electrolytes, or in mixtures of gases at low pressures or high temperatures.

We combine (1.84) and (1.88) to obtain

$$\sum_i \mu_i^{(0)}(T, P)\nu_i = -kT \ln K, \tag{7.89}$$

where the equilibrium constant K is defined by

$$K \equiv \prod_i (n_i)^{\nu_i}. \tag{7.90}$$

For example, the equilibrium constant K for the reaction in (1.79) is

$$K = \frac{(n_{H_2O})^2}{(n_{H_2})^2 n_{O_2}}. \tag{7.91}$$

The *law of mass action* states that, if the system is in equilibrium at a given temperature and pressure, then the ratio on the right-hand side of (1.91) is a constant. Given the chemical potentials $\mu_i^{(0)}(T, P)$ we can determine the equilibrium constant and predict the equilibrium concentrations.

How can the law of mass action be used? Consider the same example, but suppose that the concentrations of the various molecules are initially not in equilibrium. The initial reaction ratio is given by

$$Q = \frac{(n_{H_2O}^{(i)})^2}{(n_{H_2}^{(i)})^2 n_{O_2}^{(i)}}, \tag{7.92}$$

where the initial concentrations $n^{(i)}$ are arbitrary. If $Q > K$, then the system will produce more reactants n_{H_2} and n_{O_2}. If $Q < K$, then the system will produce more product, or water in this case.

We can also find the equilibrium concentration of the reactants and products given the initial arbitrary concentrations of just the reactants. Let x be the final equilibrium concentration of water. Then from (1.91) we have

$$K = \frac{x^2}{(n_{H_2}^{(i)} - x)^2 (n_{O_2}^{(i)} - x/2)}, \tag{7.93}$$

where $n_{H_2}^{(i)} - x$ and $n_{O_2}^{(i)} - x/2$ are the equilibrium concentrations of the reactants. We can solve (1.93) for x to obtain the equilibrium concentrations of the reactants and products.

To determine how the equilibrium constant depends on T and P we need to know how the chemical potentials of the pure substances change with T and P. We know that the chemical potential is the Gibbs free energy per particle, which is related to the enthalpy by

$$g = \mu = h - Ts, \tag{7.94}$$

where lower case indicates an intensive quantity. From the Gibbs-Duhem equation (2.158) we have that $s = -(\partial \mu / \partial T)_P$, and thus (1.94) becomes

$$\mu = h + T \left(\frac{\partial \mu}{\partial T} \right)_P. \tag{7.95}$$

We rearrange terms and divide by T^2 and obtain

$$-\frac{\mu}{T^2} + \frac{1}{T} \left(\frac{\partial \mu}{\partial T} \right)_P = -\frac{h}{T^2}, \tag{7.96}$$

which can be rewritten as

$$\frac{\partial}{\partial T}\left(\frac{\mu}{T}\right)_P = -\frac{h}{T^2}. \tag{7.97}$$

Check (1.97) by taking derivatives and obtaining (1.96).

If the form for the chemical potential given in (1.88) is applicable, we can divide (1.87) by T, take the temperature derivative, and use (1.97) to find

$$\left(\frac{\partial \ln K}{\partial T}\right)_{P,\{n_i\}} = \frac{1}{kT^2}\sum_i \nu_i h_i^{(0)}, \tag{7.98}$$

where $h_i^{(0)}$ is the specific enthalpy of the pure ith substance. Similar calculations lead to

$$\left(\frac{\partial \ln K}{\partial P}\right)_{T,\{n_i\}} = -\frac{1}{kT}\sum_i \nu_i v_i^{(0)}, \tag{7.99}$$

which gives the change in K with pressure in terms of the specific volumes $v_i^{(0)}$. If there is sufficient empirical data for the enthalpies and volumes, we can determine K at any temperature and pressure.

If the right-hand side of (1.98) is positive, the reaction is endothermic, which means that the reaction needs energy to produce the products. This energy goes into forming chemical bonds, another form of energy distinct from the kinetic energy of the molecules and the potential energy of interaction between the molecules. If we add energy to the system by heating, (1.98) indicates that $\ln K$ and thus K will increase, which will consume some of the added energy, which in turn will cool the system. Similar reasoning implies that, if the reaction is exothermic (releases energy when producing products), then an increase in the temperature will decrease the amount of the products, thus consuming energy and cooling the system. Cooling an exothermic system results in energy being produced by the reactions so as to oppose the cooling. In either case the system's behavior after a change in temperature is to oppose the change. Analogous behavior occurs for pressure changes. If we increase the pressure and the right-hand side of (1.99) is positive, the reactants will have more volume than the products (ν_i is negative for reactants and positive for products), and K will increase. An increase in K leads to more products, which in turn lowers the volume thus decreasing the pressure. In either case the system opposes the changes. This general rule is called *Le Châtelier's principle* and is analogous to Lenz's law in magnetism.

Problem 7.12. Producing ammonia

Consider the exothermic reaction that produces ammonia:

$$N_2 + 3H_2 \Leftrightarrow 2NH_3. \tag{7.100}$$
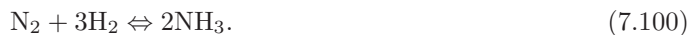
(a) Use Le Châtelier's principle to determine whether an increase in the temperature will lead to an increase or decrease in the amount of ammonia.

(b) Assume that the reactants and products in (1.100) are gases. Use Le Châtelier's principle to determine whether an increase in the pressure will produce more or less ammonia. $\square$

Vocabulary

chemical equilibrium

phase coexistence curve, phase diagram

triple point, critical point

Clausius-Clapeyron equation

enthalpy of fusion, vaporization, and sublimation

metastable state, Maxwell construction

law of mass action

Additional Problems

Problem 7.13. Climb every mountain

Use the result (1.40) to estimate the boiling temperature of water at the height of the highest mountain in your geographical region. □

Problem 7.14. Change of boiling temperature

A particular liquid boils at 127°C at a pressure of 1.06×10^5 Pa. Its enthalpy of vaporization is 5000 J/mol. At what temperature will it boil if the pressure is raised to 1.08×10^5 Pa? □

Problem 7.15. Approximate height of a hill

A particular liquid boils at a temperature of 105°C at the bottom of a hill and at 95°C at the top of the hill. The enthalpy of vaporization is 1000 J/mol. What is the approximate height of the hill? □

****Problem 7.16.** Freezing of ^{4}He

^{4}He exists in liquid form at temperatures below 4.2 K at atmospheric pressure and remains liquid down to zero temperature; helium solidifies only for pressures greater than approximately 25×10^2 Pa. An interesting feature of the liquid-solid coexistence curve is that the melting pressure is reduced slightly from its value at $T = 0$ K by approximately 20 Pa at its minimum at $T = 0.8$ K. We will see that a simple model of the liquid and solid phases of ^{4}He can explain this minimum.

(a) The properties of liquid ^{4}He are dominated by quantized sound waves (known as phonons) which satisfy the dispersion relation $\epsilon = ck$, where c is the speed of sound. Calculate the contribution of these modes to the heat capacity of the liquid at low temperatures.

(b) Calculate the low temperature heat capacity of solid ^{4}He in terms of the longitudinal and transverse sound speeds c_ℓ and c_t.

(c) Use your heat capacity results for the liquid and solid to calculate the entropy difference (per particle) $s_{\text{liquid}} - s_{\text{solid}}$ assuming a single sound speed $c \approx c_\ell \approx c_t$ and approximately equal volumes per particle $v_{\text{liquid}} \approx v_{\text{solid}} \approx v$. Which phase has the higher entropy at low temperatures?

(d) Assume a small temperature independent volume difference $\Delta v = v_{\text{liquid}} - v_{\text{solid}}$ and calculate the form of the coexistence curve. To explain the reduction of the melting pressure, which phase must have the higher density? (This problem is adapted from Kardar (2007), p. 209.) □

Problem 7.17. Determination of the function $w(T)$

Because we are interested in the pressure dependence of G for a given temperature, we need not know the function $w(T)$ in (1.57). For completeness determine the form of $w(T)$ from the relation $E = (\partial(\beta F)/\partial\beta)_V$ and the van der Waals energy equation of state [see (2.24)]

$$E = \frac{3}{2}NkT - a\frac{N^2}{V}. \tag{7.101}$$

□

Problem 7.18. Calculation of the critical exponent δ

We can calculate the critical exponent δ predicted by the van der Waals equation of state by taking $T = T_c$ and determining how the order parameter depends on the pressure difference $\tilde{P} - \tilde{P}_c$. From (1.51) we have

$$\tilde{P} - \tilde{P}_c = \frac{8\tilde{\rho}\tilde{T}_c}{3 - \tilde{\rho}} - 3\tilde{\rho}^2 - 1. \tag{7.102}$$

Let $\tilde{\rho} = \tilde{\rho}_c + \Delta = 1 + \Delta$ and $\tilde{T}_c = 1$, and show that

$$\tilde{\rho} - \tilde{\rho}_c \sim \left[(\tilde{P} - \tilde{P}_c)\right]^{1/3} \tag{7.103}$$

by placing all the terms in (1.102) over a common denominator. What is the value of δ and how does it compare to the value predicted by mean-field theory? □

Suggestions for Further Reading

Ralph Baierlein, "The elusive chemical potential," Am. J. Phys. **69**, 423–434 (2001).

— *Thermal Physics*, Cambridge University Press (1999).

Craig F. Bohren and Bruce A. Albrecht, *Atmospheric Thermodynamics*, Oxford University Press (1998). Chapter 5 of this delightful text has an excellent discussion of water and its transformations.

S. C. Colbeck, "Pressure melting and ice skating," Am. J. Phys. **63**, 888–890 (1995); S. C. Colbeck, L. Najarian, and H. B. Smith, "Sliding temperatures of ice skates," Am. J. Phys. **65**, 488–492 (1997).

Daan Frenkel and Berend Smit, *Understanding Molecular Simulation*, Academic Press, San Diego (1996). This monograph discusses the Widom insertion method and many other useful algorithms.

L. Glasser, "Equations of state and phase diagrams," J. Chem. Educ. **79**, 874–876 (2002); "Water, water, everywhere," J. Chem. Educ. **81**, 414–418 (2004).

Mehran Kardar, *Statistical Physics of Particles*, Cambridge University Press (2007).

C. Kittel, "The way of the chemical potential," Am. J. Phys. **35**, 483–487 (1967).

David Lind and Scott P. Sanders, *The Physics of Skiing: Skiing at the Triple Point*, Springer (2004). See Technote 1 for a discussion of the thermodynamics of phase changes.

Gene F. Mazenko, *Equilibrium Statistical Mechanics*, John Wiley & Sons, 2000. Our Section 1.4 is based in part on Section 2.9 of this comprehensive graduate-level text.

Horia Metiu, *Physical Chemistry: Thermodynamics*, Taylor and Francis (2006). This text has a very clear and easy to follow discussion of the thermodynamics of chemical reactions, and provides many examples of how to use chemical data.

L. M. Quintales, J. M. Alvariño, and S. Velasco, "Computational derivation of coexistence curves for van-der-Waals-type equations," Eur. J. Phys. **9**, 55–60 (1988). See also John Lekner, "Parametric solution of the van der Waals liquid-vapor coexistence curve," Am. J. Phys. **50**, 161–162 (1982).

Jan Tobochnik, Harvey Gould, and Jonathan Machta, "Understanding temperature and chemical potential using computer simulations," Am. J. Phys. **73** (8), 708–716 (2005).

James D. White, "The role of surface melting in ice skating," Physics Teacher **30**, 495–497 (1992).