Chapter 10
Phase equilibrium

It is a familiar fact that pure substances tend to exist in one of three distinct states: solid, liquid, and gas. Take water, for example. As ice is heated at atmospheric pressure, it suddenly melts into liquid at a specific temperature. As the liquid continues to be heated, it eventually reaches a temperature at which it spontaneously vaporizes into a gas. These transitions are discontinuous, i.e., they occur at specific state conditions—particular combinations of T and P. At exactly those conditions, the system can exist in more than one form such that two (or more) phases are in equilibrium with each other.

Although we are typically familiar with phase behavior at atmospheric pressure, most substances experience a diverse set of phases over a broad range of pressures. Pure substances often have more than one crystal phase, depending on the pressure. Figure 10.1 shows a schematic of a P-T c g fkci c of water that illustrates the kind of complex phase behavior that can exist. In the case of mixtures, there are even more possibilities for phase equilibrium: for example, one can have equilibrium between two liquids of different compositions, or among multiple solid and liquid phases.

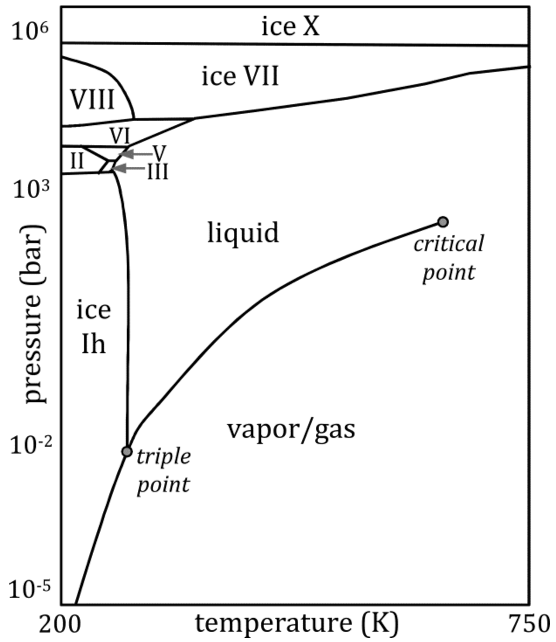

Figure 10.1. A schematic of the phase diagram of water. At greatly elevated pressures, several crystallographically distinct ice phases are seen beyond the usual ice Ih formed at ambient pressure.

In this chapter, we will address the two most important questions in the discussion of phases. First, what are the thermodynamic conditions for phase equilibrium? Second, why do phases change discontinuously? For example, why does water have a definite boiling point temperature at ambient pressure? We will use both classical thermodynamics and statistical mechanics to answer these questions.

10.1 Conditions for phase equilibrium

We must start by giving a precise definition to the meaning of "phase":

> A **phase** is homogeneous region of matter in which there is no spatial variation in average density, energy, composition, or other macroscopic properties.
>
> Phases can also be distinct in their molecular structure. For example, water has multiple ice phases that differ in their crystallographic structure.
>
> A phase can be considered a distinct "system" with boundaries that are interfaces with container walls or other phases.

The notion of phase equilibrium means that there are two or more phase "systems" present. These systems exist spontaneously on their own without the use of partitions or membranes or other interventions, and since they are in mutual equilibrium, they can exchange energy, volume, and particles. We have seen in Chapter 4 that when such is the case, the conditions of equilibrium are given by maximization of the entropy subject to the constraints of constant total energy, volume, and particles. For two phases involving a single-component, this becomes,

$$\max[S_1(E_1, V_1, N_1) + S_2(E_2, V_2, N_2)] \tag{10.1}$$

At a maximum, we have,

$$\begin{gathered} dS_1 + dS_2 = 0 \\ \frac{1}{T_1} dE_1 + \frac{P_1}{T_1} dV_1 - \frac{\mu_1}{T_1} dN_1 + \frac{1}{T_2} dE_2 + \frac{P_2}{T_2} dV_2 - \frac{\mu_2}{T_2} dN_2 = 0 \end{gathered} \tag{10.2}$$

where we used the fundamental entropy equation. Because $dE_1 + dE_2 = 0$, $dV_1 + dV_2 = 0$, and $dN_1 + dN_2 = 0$ by the constancy of the total energy, volume, and number of particles, this becomes,

$$\left(\frac{1}{T_1} - \frac{1}{T_2}\right) dE_1 + \left(\frac{P_1}{T_1} - \frac{P_2}{T_2}\right) dV_1 - \left(\frac{\mu_1}{T_1} - \frac{\mu_2}{T_2}\right) dN_1 = 0 \tag{10.3}$$

Recognizing that dE_1, dV_1, and dN_1 can all vary independently, the conditions for equilibrium between two phases must then be given by,

$$T_1 = T_2 \qquad P_1 = P_2 \qquad \mu_1 = \mu_2 \tag{10.4}$$

It will be helpful to take the following viewpoint: imagine that we can manipulate each phase independently by changing temperature, pressure, and chemical potential while retaining the same phase identity (e.g., liquid or vapor). As an example, consider liquid water and ice phases, each which might be varied in temperature and pressure. To find the conditions of solid-liquid equilibrium, we must search (T, P) space for states satisfying the equalities in (10.4). The points along which these are satisfied then correspond to the melting line. If the equalities are not met, then only one phase will exist at those state conditions.

In fact, one of the equalities in (10.4) is redundant. Recall that only two intensive variables are required to completely specify the thermodynamic state and hence all intensive properties of a single-component system. Therefore, if we choose T and P then μ for either phase is uniquely specified, and generally we can write $\mu = \mu(T, P)$. So if we are looking for T and P combinations that enable equilibrium between liquid water and ice, we can simply solve the following equation,

$$\mu_1(T, P) = \mu_2(T, P) \tag{10.5}$$

where the numbers indicate each phase. Notice that we have already accounted for the thermal and mechanical equilibrium conditions by assuming the temperatures and pressures are constant. This equality of chemical potentials constitutes an equation with two unknown, T and P. If we specify the temperature, we can solve for the pressure corresponding to phase equilibrium, and vice versa.

Eqn. (10.5) indicates that only g intensive variable is needed to specify the state of the system when two phases are in equilibrium, in a single-component system. If T is specified, then P can be found by solving the chemical potential equality, and vice versa. This reduction in the number of independent degrees of freedom occurs because the mere fact that two phases coexist provides a constraint on the chemical potentials. Fig. 10.2 illustrates the procedure graphically, with the chemical potential in arbitrary units.

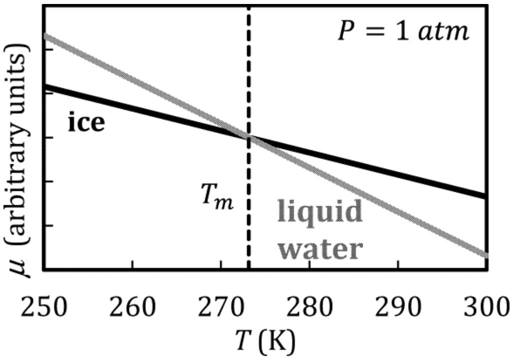

Figure 10.2. Schematic of the temperature-dependence of the chemical potentials of liquid water and ice at ambient pressure. At 273 K, the chemical potentials are equal and phase equilibrium occurs. Above (below) that temperature, liquid water (ice) has the lower chemical potential and is the thermodynamically stable phase.

From Fig. 10.2, we can see that there is only one temperature at which the chemical potentials of the liquid and crystal are equal. That is the temperature of phase equilibrium at this pressure, here the melting temperature T_m. Below T_m, the crystal has a lower chemical potential. Because the thermodynamic potential minimized at constant T and P is the Gibbs free energy G, and since $G = N\mu$ for a single component system, the crystal is therefore the only phase present at $T < T_m$. Under those conditions, it is the most stable state of the system at equilibrium, as any liquid would increase the free energy. Similarly for $T > T_m$, the liquid is the only phase present.

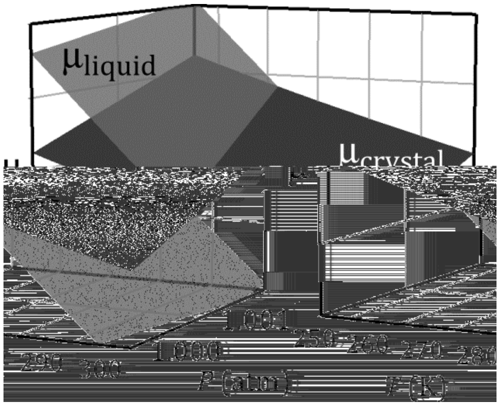

Fig. 10.3. Schematic of the temperature and pressure dependencies of the chemical potential of ice and liquid water. The intersection of the two surfaces defines a melting line when projected onto the T-P plane (the floor of this graph).

If we consider variations in both temperature and pressure, then we must consider the chemical potentials in a three-dimensional space, as illustrated in Fig. 10.3. The intersection of the two chemical potential surfaces then defines a line in the T-P plane along which phase equilibrium can occur. This line is the melting line, and we can express it as either $P_m(T)$ or $T_m(P)$.

What if three phases are in equilibrium, in a single component system? In that case, two equalities of chemical potentials must be satisfied, $\mu_1 = \mu_2$ and $\mu_2 = \mu_3$ (the equation $\mu_1 = \mu_3$ is clearly redundant). This amounts to two equations and two unknowns, T and P. Since there are no free variables, the temperature and pressure must be exactly specified in discrete solutions. This is why the triple point of a material—at which solid, liquid, and gas phases all coexist—is a point in the T-P plane, and not a line.

These simple examples illustrate some basic features of phase equilibrium:

> At constant T and P in a single-component system, the phase that is observed is the one that has the lowest Gibbs free energy per particle, or equivalently, the lowest chemical potential $\mu(T, P)$. At conditions where the chemical potentials of two or more phases are equal and at a minimum with respect to all other phases, the former can coexist in equilibrium with each other.

Of course, we can generalize these ideas in a mathematical framework that describes any kind of phase equilibrium, for arbitrary multicomponent systems. Consider the case in which there are n_{phase} phases and C components. There are C chemical potentials in each phase that depend not only on T and P, but on all of the compositions of their respective phases as well, $\{x\} = (x_1, x_2, \dots, x_C)$ where x denotes mole fraction. Note that only $C - 1$ mole fractions are independent in each phase since they must always sum to unity. The conditions for equilibrium can then be cast as,

$$\begin{gathered}\mu_{\text{component } i, \text{ phase } k}\left(T, P, \{x\}_{\text{phase } k}\right) = \mu_{\text{component } i, \text{ phase } k+1}\left(T, P, \{x\}_{\text{phase } k+1}\right) \\ \text{for all } i = 1,2,\dots,C \quad \text{and} \quad k = 1,2,\dots,n_{\text{phase}} - 1\end{gathered} \tag{10.6}$$

There are $C(n_{\text{phase}} - 1)$ total such equations and $2 + n_{\text{phase}}(C - 1)$ independent variables from T, P, and the $C - 1$ independent mole fractions in each phase. The number of degrees of freedom in this problem, n_{DOF}, is given by the total number of variables minus the number of chemical potential constraint equations,

$$\begin{aligned} n_{\text{DOF}} &= 2 + n_{\text{phase}}(C - 1) - C\left(n_{\text{phase}} - 1\right) \\ &= C - n_{\text{phase}} + 2 \end{aligned} \tag{10.7}$$

This is the famous *c g g*, originally derived by Gibbs. Though we derived it on mathematical grounds, its physical interpretation is:

> **Gibbs' phase rule** asserts that the state conditions giving rise to equilibrium among n_{phases} in a C-component system are exactly characterized by n_{DOF} *ce e ke k g k g* degrees of freedom, where $n_{\text{DOF}} = C - n_{\text{phase}} + 2$. That is, only n_{DOF} pieces of information are required to uniquely specify the state of the entire system, knowing that n_{phases} are present. These pieces of information are typically drawn from T, P, and the phase compositions.

Consider the space of the variables T, P, and the set of compositions. Let us imagine the ways in which different values of n_{DOF} are manifested in this space. In the case $n_{\text{DOF}} = 0$, there are no free variables and phase equilibrium corresponds to single, discrete sets of state conditions. These are points in the P-T diagram for single-component systems. For $n_{\text{DOF}} = 1$, state variables can move in concert with one another along one direction in state space, such as a line in the single-component P-T diagram. Finally with $n_{\text{DOF}} = 2$, there is flexibility to move in two independent directions in the parameter space. For a single-component system, this corresponds to an area in the P-T plane.

The phase rule just described applies to non-reactive systems. If a set of components can interconvert by way of a reversible chemical reaction that also reaches equilibrium, then the phase rule is modified:

$$n_{\text{DOF}} = M - n_{\text{phase}} + 2 - n_{\text{reaction}} \tag{10.8}$$

where n_{reaction} is the number of such equilibrium reactions. It might be easy to see why there is a reduction in the degrees of freedom: for each reaction, there is an additional constraint equation that relates the concentrations of different components to an equilibrium constant. More technically, chemical reactions add additional chemical potential equalities, as discussed later in Chapter 20.

10.2 Implications for phase diagrams

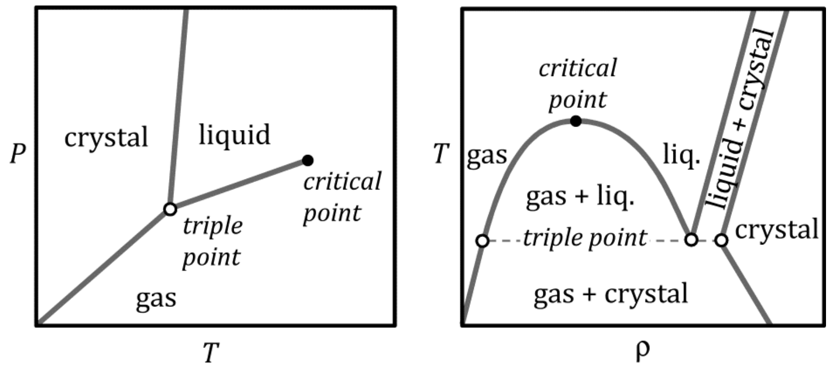

Figure 10.4. Schematics of typical phase diagrams for simple, single-component systems (e.g., argon). In the P-T diagram to the left, single phases appear as areas, while phase equilibrium occurs along lines and at points. In the T-ρ diagram to the right, both single phases and two-phase equilibria appear as areas. In two-phase conditions, the density ρ corresponds to the overall system density, that is, the total moles divided by the total volume of both phases. At a given temperature, therefore, a horizontal line intersecting the boundaries surrounding a two-phase region gives the individual densities of the coexisting phases.

A common way to depict the conditions giving rise to phase equilibrium is through a *c g fkci c* . Indeed there are many kinds of phase diagrams, but two examples typical for a single-component system are shown in Figure 10.4. In the P-T diagram, lines correspond to regions with two phase-equilibrium. It is easy to see that $n_{\text{DOF}} = 1$ along these lines, since the indication of temperature automatically specifies the pressure, and vice versa. On the other hand, $n_{\text{DOF}} = 0$ corresponds to a point, such as the triple point.

An alternative representation of the same behavior is shown in the T-ρ diagram in Fig. 10.4. This depiction differs in an important respect: two-phase regions correspond to areas rather than lines because the density changes discontinuously as one moves from one phase to another. For example, if a liquid is heated at constant pressure, it will eventually begin to vaporize at the boiling temperature. For a small amount of heat added, the system consists of a minuscule amount of gas at low density and a large amount of liquid at high density, for an *g c* system density that remains close to that of the liquid. However, as more heat is added, the moles in the gas phase increase at the expense of those in the liquid; while the individual densities of these phases remains the same, the overall density is thus shifted towards that of the gas. It is this overall density that is represented on the x-

axis of T-ρ diagrams within the two-phase areas, while the boundary lines give the densities of the individual phases.

The slopes of boundaries in phase diagrams are tightly connected to thermodynamic properties. Consider the liquid-gas boundary in the P-T diagram. Along this line the chemical potentials of both phases must be equal; otherwise, two-phase equilibrium would not be possible. Therefore, if we move a short distance along the liquid-gas boundary, the chemical potentials of the liquid and gas must change by exactly the same amount since they must continue to be equal at the ending point. In the limit of an infinitely small change,

$$d\mu_L(T,P) = d\mu_G(T,P) \qquad \text{(along phase boundary)} \tag{10.9}$$

Taking the full differential of μ and recognizing that $\mu = g$ for a single component,

$$-s_L dT + v_L dP = -s_G dT + v_G dP \qquad \text{(along phase boundary)} \tag{10.10}$$

Rearranging and completing the derivative,

$$\left(\frac{dP}{dT}\right)_{\text{phase boundary}} = \frac{s_G - s_L}{v_G - v_L} = \frac{\Delta s}{\Delta v} \tag{\textbf{10.11}}$$

Eqn. (10.11) asserts that the slope of the liquid-gas boundary in the P-T phase diagram is related to the molar entropy and volume differences of the two phases. Actually, this equation is valid for c phase boundary because

The reader is encouraged to perform the full derivation of Eqn. (10.13) themselves. Finally, in cases where the enthalpy difference does not vary significantly with temperature, we can treat Δh as constant and integrate to obtain,

$$\ln \frac{P_2}{P_1} = -\frac{\Delta h}{k_B}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \tag{10.14}$$

where (T_1, P_1) and (T_2, P_2) are two points on the liquid-gas phase boundary. If we treat T_1 and P_1 as reference "constants," this equation could also be written in the form that gives the saturation pressure at any temperature,

$$\ln P_{\text{sat}}(T) = c_1 - \frac{c_2}{T} \tag{10.15}$$

where $c_1 = \Delta h_{\text{vap}}/k_B T_1 + \ln P_1$ and $c_2 = \Delta h_{\text{vap}}/k_B$ are treated as constants. The form of this equation is remarkably similar to empirically-fitted correlations used to predict the saturation pressure, such as the *C k gg c k*

$$\ln P_{\text{sat}}(T) = c_1 - \frac{c_2}{c_3 + T} \tag{10.16}$$

The additional constant c_3, relative to (10.15), compensates for the assumption of a constant enthalpy of vaporization. Eqn. (10.16) is widely-used in practice and values for c_1, c_2, and c_3 for a large number of liquids are available in many reference texts and publications.

For equilibrium between solids and gases—sublimation—we can also use the Clausius-Clapeyron equation because the gas volume remains much greater than that of the crystal. However, for solid-liquid or solid-solid equilibrium, one must return to the original Clapeyron equation since this assumption becomes poor.

EXAMPLE 10.1

C g ge mg k cd g e mh f c kf d g cd k i c g g ck k c k kf c gc g g gc g c kd gc c g ke e fkk c e c g gd kk i g gc g h c g k c g ge mg c gf c kcd gc g ke g g gg c h c kc k h c g c c dkg e fkk k $\Delta h = 40.7$ *kJ/mol*

To address this problem, we use the integrated Clausius-Clapeyron equation of (10.14):

$$\frac{14.7\text{ psi} + 15\text{ psi}}{14.7\text{ psi}} = exp\left[-\frac{40700\text{ J/mol}}{8.31\text{ J/mol/K}}\left(\frac{1}{T_2} - \frac{1}{373\text{ K}}\right)\right]$$

Solving for T_2,

$$T_2 = 393\ K = 120\ ^\circ C$$

10.3 Other thermodynamic behaviors at a phase transition

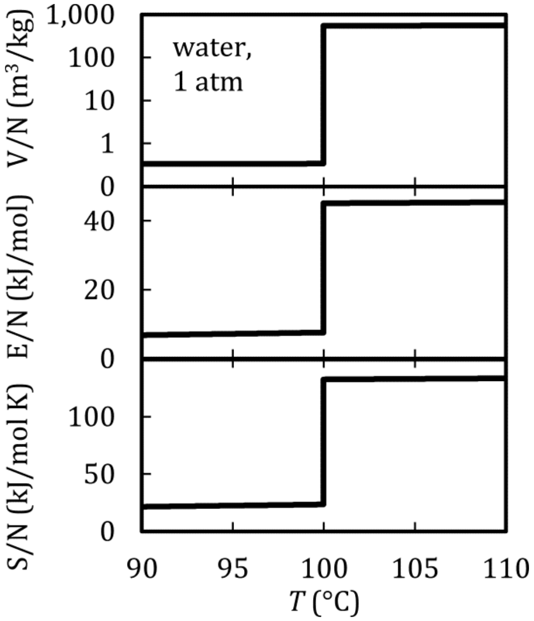

Figure 10.5. Extensive properties—and per mole or per mass versions thereof—change discontinuously at the liquid-vapor phase transition. Illustrated here is the behavior of the volume, internal energy, and entropy for water under atmospheric pressure.

At a phase transition, the second law demands that the chemical potentials, temperatures, and pressures of the phases present are equal, but what about differences in other properties such as the entropy, energy, and volume? In general, these variables change *fke k* across a phase transition. Figure 10.5 illustrates this behavior for the liquid-vapor transition in water at atmospheric pressure. Clearly at $T = 100$ °C, there are discontinuous changes in the volume, entropy, and energy. In other words, $\Delta v, \Delta s$, and Δe can take on nonzero values that are characteristic of the boiling point.

Similarly, the change in enthalpy, $\Delta h = \Delta e + P\Delta v$, is also discontinuous. This is a particularly important quantity because the first law at constant pressure gives $Q = \Delta H$, which implies that heat added to a system at phase equilibrium is directly related to the system enthalpy change. We typically term the quantity Δh the *c g gc* or *c g g c* of a given phase transition; in the water example, it is the latent heat of vaporization.

How then does the intensive heat capacity, $c_P = (dh/dT)_P$, behave at a phase transition? If the enthalpy changes discontinuously at the boiling point, then c_P diverges. The heat and hence enthalpy added to the system at the boiling temperature converts liquid into vapor, rather than increases the system temperature. In other words, the enthalpy of vaporization is absorbed with zero change in temperature, which suggests the lack of a well-defined heat capacity.

the expense of the liquid, at constant temperature. This is in contrast with the pure liquid and gas phases, in which the temperature rises with increases in enthalpy.

Figure 10.6 illustrates the relationship of system to individual phase properties using water and its enthalpy as an example. For a constant pressure process, the first law $Q = \Delta H$ shows that heating water below its boiling point increases its enthalpy and raises the liquid temperature until it reaches 100 °C. At that point, the system is pure liquid water with an infinitesimally small amount of vapor. As heat is further added, the temperature remains constant but the amount of vapor grows until eventually the entire system consists of vapor and an infinitesimally small amount of liquid. As might be obvious, this occurs when heat in the amount of the enthalpy of vaporization is added. During vaporization, all of the properties of the liquid and gas phases remain constant: their densities, molar energies and entropies, etc. Finally, after the last drop of liquid has vanished, additional heat raises the temperature and increases the enthalpy of the homogeneous gas phase.

EXAMPLE 10.2

C c ke c gcff gc ci c h cgc gcgh C g c gcgh gc ki k g i c g cg ec ck ck c gc g kkd k cg h g cg k k kkc c g gc g k k cmg gk kf e gg d k hh

Assuming constant atmospheric pressure for the process, we have for the water,

$$dE = \delta Q + \delta W = \delta Q - PdV$$

$$\delta Q = dE + PdV \qquad \rightarrow \qquad Q = \Delta E + P\Delta V = \Delta H$$

The work is nonzero because the water will expand against the pressure of the atmosphere as it is heated and changed into a gas. Thus, the heat added from the microwave increases the water's enthalpy. Because enthalpy is a state function, we can calculate the total change in H between the liquid and gas using a cycle by which we heat the liquid and then boil it. The total enthalpy is calculated as follows, assuming constant heat capacity for the liquid,

$$\begin{aligned} \Delta H &= N c_p (T_H - T_C) + N \Delta h_{\text{boil}} \\ &= N(4.19 \text{ J/mol K} \times 80 \text{ K} + 40600 \text{ J/mol}) = N(40900 \text{ J/mol}) \end{aligned}$$

For a typical glass of water, $N = 13$ mol. Thus,

$$t = \frac{\Delta H}{\dot{Q}} = \frac{(13 \text{ mol})(40900 \text{ J/mol})}{500 \text{ J/s}} = 1060 \text{ s} = 18 \text{ min}$$

10.4 Types of phase equilibrium

The considerations above show that a phase change often involves a discontinuity in enthalpy and volume. There are, however, special phase transitions where the changes in enthalpy and volume are exactly zero. These are often called *ge f fg c g*

$c \quad kk$, an old nomenclature originated by Paul Ehrenfest. In this classification scheme, phase transitions are characterized by the free energy derivatives that change discontinuously. Consider the chemical potential in a single component system, for which $\mu = g$. $k \quad fg \quad c \ g \ c \quad kk$ occur when discontinuities arise in its first derivatives, $\partial\mu/\partial T = -s$ and $\partial\mu/\partial P = v$. These are the most common phase transitions, and are generally of the familiar type, such as melting, boiling, sublimation, liquid-liquid separation, etc. On the other hand, second order phase transitions have first derivatives (s, v) that remain continuous, but entail discontinuities in the second derivatives, $\partial^2\mu/\partial T^2 = -\partial s/\partial T = -c_P/T$, $\partial^2\mu/\partial P^2 = \partial v/\partial P = -v\kappa_T$, $\partial^2\mu/\partial T\partial P = \partial v/\partial T = v\alpha_P$. In other words, second order phase transitions involve discontinuities in the response functions c_P, κ_T, and α_P.

The Ehrenfest scheme is generally useful for describing a large range of different kinds of phase transitions. However, the modern notion of a phase transition's "order" has taken on more subtle definitions. Generally in the modern context, a first order transition is one that involves a nonzero latent heat Δh. Second order transitions, on the other hand, are characterized by the behavior of molecular-scale correlations and how they scale as one approaches the transition. Such analyses are the province of modern research in statistical mechanics, and are thus beyond the scope of this book. However, it is useful to recognize that such transitions indeed exist, occurring in magnetic materials, superfluids, and liquid crystals, for example. In addition, the liquid-gas transition at the critical point becomes second order where differences between the gas and liquid vanish and it becomes possible to continuously change between them, with no discontinuities.

10.5 Microscopic view of phase equilibrium

So far, we have said nothing about why phase transitions exist. After all, a system of molecules doesn't know that it needs to change abruptly to a gas at a well-defined boiling temperature. The system instead knows only the fundamental atomic interactions governing the time evolution of its constituent molecules. Therefore, the observation that a system can spontaneously phase separate into two distinct regions is a $e \quad g \quad g \ eg$ of the nature of molecular interactions, not a separate feature of the molecular world. Phase transitions, it turns out, emerge in the limit of very large systems of molecules.

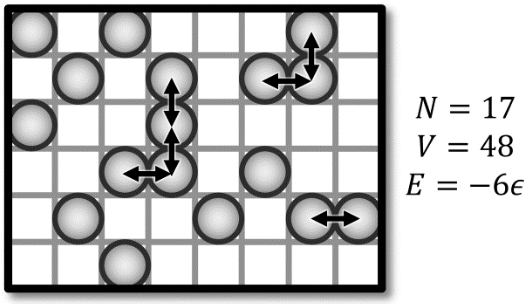

Figure 10.7. Schematic of the lattice gas model in two dimensions. Molecules cannot overlap and those that are nearest neighbors experience an attractive interaction in the amount of $-\epsilon$. A central molecule has four (six) nearest neighbors in 2D (3D).

To illustrate this point, it helps to examine a model of molecular interactions. One of the simplest we can study is the so-called *c kegi c fg*, a very basic approach to the liquid-gas transition. The model postulates that the volume available to molecules is subdivided into small cells that form, for instance, a cubic lattice. Each cell is the size of a single molecule, and can either contain one or not. When two molecules sit adjacent to each other in neighboring cells, they experience an attractive potential energy in the amount of $-\epsilon$. The approach is illustrated in two dimensions in Figure 10.7.

Though it does not describe the atomic world in quantitative detail, the lattice gas captures the two most important features of all liquids and gases. First, molecules experience an attractive interaction upon close approach, typically due to van der Waals forces, which are present in every molecular system. Second, molecules have some *ceg* in which to move around depending on the density of the system, here in terms of the number of molecules per the number of lattice sites. Although this model seems very crude, these features capture the main physical driving forces behind the liquid-gas transition. In fact, near the critical point, a huge range of substances behave *g ce* like the lattice gas. This surprising result is called *k g c k*, and it was discovered and developed in the 1960s and 1970s.

Moreover, the lattice gas model is useful for describing other phase transitions. In particular, if instead of particles in the lattice one considers magnetic spins, the model reproduces the ferromagnetic behavior of materials like iron. In fact, the model was originally introduced for this purpose in 1925 by Ernst Ising in his Ph.D. thesis, and hence is often called the *k i fg*.

To understand the origins of liquid-vapor phase behavior, we must develop the thermodynamic properties of this model by determining a thermodynamic potential that is a function of its natural variables, like $S(E,V,N)$, $E(S,V,N)$, or $G(T,P,N)$. For one and two dimensions, the lattice gas is exactly solvable. The one dimensional case is fairly easy to derive and can be found in standard statistical mechanical texts. The two dimensional case is far more complicated. It wasn't until 1944 that Lars Onsager, a chemical engineer-turned-chemist at Yale, determined the mathematical solution to the 2D Ising model that later won him the Nobel Prize. For three dimensions, it is quite possible that there are analytical solutions.

Rather than seek an exact solution, here we will find an approximate one that has the same basic features as the true one. We will compute the Helmholtz free energy using the equation,

$$A = E - TS \tag{10.19}$$

First, we find the average energy we expect for putting N lattice gas molecules randomly in a volume V. The random part is an approximation, since attractive interactions certainly could coax molecules into very non-random, clustered configurations. On the lattice, each molecule has z neighbors, where $z = 6$ in three dimensions. If we focus on one molecule, we can approximate the number of neighbors that it has, on average, by assuming the density among the neighbors is the same as the bulk density. Thus the average number of neighbors to a molecule is $z \times (N/V)$. The total energy contributed by that molecule is,

$$E_{\text{molecule}} \approx -\frac{1}{2}\left(z\frac{N}{V}\right)\epsilon \tag{10.20}$$

The half stems from the fact that each pair interaction must be shared between two molecules, with $-\epsilon/2$ given to the central one and $-\epsilon/2$ to the neighbor. This particular simplification is called the *gc hkg f c k c k* because we have assumed an average density and energy field surrounding each molecule, rather than performed a detailed enumeration of specific configurations. The mean-field approach is an extremely common way of evaluating statistical mechanical models because it obviates the need to consider configurations explicitly. Finally, the total system energy is N times that of (10.20),

$$\begin{aligned} E &= NE_{\text{molecule}} \\ &= -\frac{\epsilon z}{2}\left(\frac{N^2}{V}\right) = -\frac{\epsilon z}{2}\rho^2 V \end{aligned} \tag{10.21}$$

where the number density is $\rho = N/V$. The next task is to compute the entropy term of (10.19) by counting configurations. We have no need to consider energies because the mean field approximation assumes that all configurations have the same energy, that of (10.21). Thus, for V lattice sites and N molecules, the number of ways to arrange them is,

$$\Omega = \frac{V!}{N!\,(V-N)!} \tag{10.22}$$

Taking the logarithm and applying Stirling's approximation, we obtain,

$$S = k_B \ln \Omega = -k_B V[\rho \ln \rho + (1-\rho)\ln(1-\rho)] \tag{10.23}$$

Putting both Eqns. (10.21) and (10.23) both parts together allows us to determine the free energy per particle,

$$\frac{A}{N} = -\frac{\epsilon z}{2}\rho + k_B T \rho^{-1}[\rho \ln \rho + (1-\rho)\ln(1-\rho)] \tag{10.24}$$

To understand the behavior of this model as a function of temperature and pressure, we construct the per-particle Gibbs free energy, $g(T,P) = G(T,P,N)/N$. This is given by the Legendre transform,

$$\begin{aligned} g(T,P) &= \frac{A}{N} + \frac{PV}{N} \\ &= -\frac{\epsilon z}{2}\rho + k_B T \rho^{-1}[\rho \ln \rho + (1-\rho)\ln(1-\rho)] + P\rho^{-1} \end{aligned} \tag{10.25}$$

Recall that the Gibbs free energy is at a minimum at equilibrium, for constant T and P conditions. Therefore, the equilibrium density for a particular T and P is given by the value of ρ that minimizes this expression. This is equivalent to the statement that we find a value of ρ that minimizes $g(T, P)$ per the recipe for a Legendre transform.

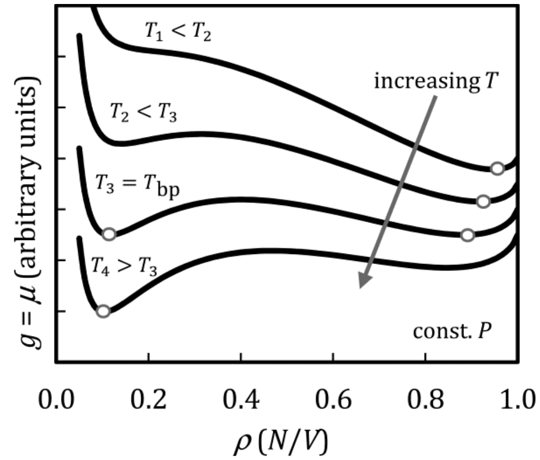

Figure 10.8. Behavior of the per-particle Gibbs free energy of the lattice gas model, for different temperatures at constant pressure. Two minima appear with respect to density: at low temperatures, the global minimum corresponds to liquid-like densities, while at high temperatures, it occurs at gas-like ones. Each curve is shifted vertically by an arbitrary amount for clarity.

The density-dependence of Eqn. (10.25) at constant pressure and for three dimensions ($z = 6$) is illustrated in Fig. 10.7. It is clear that there are two local minima in the free energy with respect to density, but their behavior is highly temperature-dependent. At low T, the minimum at higher densities is lowest, implying that it is the dominant, minimum free energy at equilibrium. This is the liquid. In contrast at high T, a low-density minimum is the globally extremum; this is the gas. At a particular intermediate temperature, the depth of the two minima are equal and the system can experience both states at equilibrium. This special state is the boiling temperature, T_{bp}.

These considerations explain why a liquid changes discontinuously into a gas when heated at constant pressure: the gas state suddenly becomes the global free energy minimum. Why are there two distinct minima in the free energy curve? Qualitatively, it is because distinct physical interactions dominate the behavior of each state. Liquids experience favorable energetic interactions because molecules are in close contact, and van der Waals forces contribute attractive (negative) energies. Gases have large entropies since they afford molecules a large volume in which to roam. As the liquid is heated, the drive to gain entropy overwhelms the favorable energetic interactions. Consider that the Gibbs free energy, $G = H - TS$, shows that as T increases the entropic eventually term becomes more important than the enthalpic one.

Figure 10.9. The free energy curves for several representative state points in the P-T and T-ρ phase diagrams of the top two panels are illustrated in the bottom ones. At coexistence, the liquid and gas minima have equal depth, but the barrier between them shrinks and eventually disappears as one approaches the critical point (c.p.). Above this point, the system is a supercritical fluid, with no distinction between liquid and gas.

Of course, the free energy curves and hence boiling temperature in Fig. 10.8 would change with pressure. In general, if we were to examine these curves across the entire P-T phase diagram, we would see bahavior reminiscent of Fig. 10.9. Notice that the locus of points for which the two minima have equal depth forms a line in the P-T diagram. This boundary could be called the boiling line, the saturation curve, or the liquid-vapor equilibrium line. As one moves from low to high temperatures along this boundary, the barrier between the two minima decreases. Eventually at the *e kkec k*, the barrier disappears altogether. Above P_c and T_c, there is only one minimum in the free energy, corresponding to a supercritical fluid, and there is no longer a distinction between liquid and gas.

Why is there a free energy barrier that separates the two minima in the free energy function? Physically, the barrier is related to the penalty paid for the existence of a surface that separates the two phases present. It is therefore an unfavorable increase in free energy due to a *hceg g k* relevant to intermediate densities that lie between the liquid and gas. At coexistence, the two phases attempt to minimize the surface area to minimize the free energy.

> For a single-component liquid-gas transition, there are two minima in the Gibbs free energy as a function of density. The stable phase corresponds to the lowest-lying minimum at a given T and P. The boiling or saturation line

corresponds to the locus of (T, P) points along which the two minima are of equal depth, separated by a free energy barrier. The critical point is the temperature and pressure at which the barrier vanishes, above which there is only one free energy minimum for the supercritical fluid.

It is relatively easy to compute the coexistence densities from the model. One approach is to simply tune T (or P) at fixed P (or T) until the minima predicted by Eqn. (10.25) are of equal dept. Frequently, however, we do not have direct access to this function, but rather some simpler experimentally-fit model like the equation of state. In the lattice gas, the latter is given by,

$$\begin{aligned} P &= -\left(\frac{\partial A}{\partial V}\right)_{T,N} \\ &= -N\left(\frac{\partial \rho}{\partial V}\right)\left(\frac{\partial (A/N)}{\partial \rho}\right) = \rho^2\left(\frac{\partial (A/N)}{\partial \rho}\right) \\ &= -\frac{\epsilon z}{2}\rho^2 - k_B T \ln(1-\rho) \end{aligned} \tag{10.26}$$

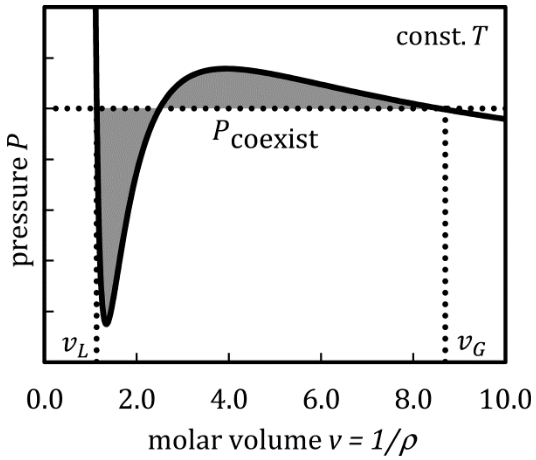

Figure 10.10. The equation of state ($P(T, v)$) shows a van der Waals type loop with molar volume at fixed pressure, indicating the presence of liquid-vapor equilibrium. The equal area construction is used to determine the coexistence pressure and molar volumes (and hence densities) at this temperature.

One can determine whether or not an equation of state predicts coexistence by examining its dependence on molar volume, $v = 1/\rho$, at constant temperature. Figure 10.10 illustrates this behavior in the lattice gas. We see that the pressure displays a kind of non-monotonic behavior, which is actually an artifact of the mean-field approximation. In reality, the pressure should display a flat line at the densities in the coexistence region, i.e., in between the liquid and gas volumes v_L and v_G. Such a behavior would correspond to the discontinuous change in molar volume as the pressure crossed the melting line at a given temperature. This would have been the behavior if we had performed an exact evaluation of the model in the large-system limit rather than employed the mean-field approximation.

The non-monotonic behavior of the kind in Fig. 10.10 is termed a *c fg cc* , and it is frequently encountered in approximate or empirical equations of state. To find the coexistence pressure and densities, one uses the *g c c gc e e k* as illustrated. We shall now derive this rule. The chemical potentials of the liquid and gas must be equal at coexistence, $\mu_G = \mu_L$; therefore, the chemical potential difference as we integrate across molar volume at constant temperature from gas to liquid must be zero, $\Delta\mu = 0$. Recalling that $(\partial\mu/\partial P)_T = v$ for a single-component system, we can write,

$$\Delta\mu = 0 = \int_{P_\mathrm{L}}^{P_G} v dP \tag{10.27}$$

Using the chain rule, $d(Pv) = vdP + Pdv$,

$$0 = \Delta(Pv) - \int_{v_\mathrm{L}}^{v_G} P dv \tag{10.28}$$

Since the integration limits are at the same, coexistence pressure, we finally have,

$$P_\mathrm{coexist}(v_G - v_L) = \int_{v_\mathrm{L}}^{v_G} P dv \tag{10.29}$$

Eqn. (10.29) is simply another way of saying that the shaded areas in Fig. 10.10 must be equal: the total area under the curve should be equal to the area of the box formed between the x-axis endpoints v_G and v_L, and between 0 and P_coexist on the y-axis. This can only happen if the shaded areas exactly balance.

The critical temperature occurs when the pressure no longer exhibits the non-monotonic behavior shown in Fig. 10.10. At this state, the minimum and maximum in the pressure converge to the same point as an inflection point. Thus, at the critical point,

$$\left(\frac{\partial P}{\partial \rho}\right)_T = 0 \quad \text{and} \quad \left(\frac{\partial^2 P}{\partial \rho^2}\right)_T = 0 \tag{10.30}$$

Substituting Eqn. (10.26),

$$-\epsilon z \rho + \frac{k_B T}{1-\rho} = 0 \quad \text{and} \quad -\epsilon z + \frac{k_B T}{(1-\rho)^2} = 0 \tag{10.31}$$

These two equations can be solved simultaneously for ρ and T, giving for the critical density and temperature,

$$\rho_c = \frac{1}{2} \quad \text{and} \quad T_c = \frac{1}{4}\frac{\epsilon z}{k_B} \tag{10.32}$$

These results can then be back-substituted in (10.26) to find the critical pressure,

$$P_c = \epsilon z \left(\frac{\ln 2}{4} - \frac{1}{8} \right) \tag{10.33}$$

In three dimensions $z = 6$ and the critical temperature is $T_c = 1.5\epsilon/k_B$. The mean-field approximation actually overestimates the true critical parameters here; for example, detailed computer simulations have established the critical temperature to exist near $T_c = 1.12\epsilon/k_B$.

10.6 Order parameters and general features of phase equilibrium

In the preceding section, we examined phase equilibrium in the liquid-vapor case using a Gibbs free energy function dependent on the density. In general for any kind of phase equilibrium, one needs to consider the behavior of a free energy as a function of some *fg c c g g* that distinguishes between the two phases. For the liquid-vapor transition, a natural order parameter is the density. However, this is not always the most useful metric to choose. For example, in solid-liquid transitions, the density difference can be very small, or even zero, and thus we might need a rather order parameter, such as a crystalline lattice metric that quantifies the structural behavior of the molecules. For multicomponent mixtures, often the compositions (e.g., mole fractions) are useful as order parameters since the mixture might phase-separate into regions enriched in various components.

Once one or more appropriate order parameters are identified, the procedure is to examine a free energy expressed as a function of them in addition to its natural variables. Then, the stable phase corresponds to the values of the order parameters that minimize the free energy. If we were to find conditions for which more than one global minima exist, then these conditions correspond to phase equilibrium. It is possible that more than two global minima may be present. This occurs in a single component system at its triple point. In multicomponent systems, the possibilities for multiple minima increase, per Gibbs' phase rule. For example, two immiscible liquid phases can be in equilibrium with a vapor phase; in this case, we would seek three global free energy minima in the multidimensional space of both density and composition.

Problems

Conceptual and thought problems

1. A liquid mixture of 1-propanol and 1-pentanol is prepared under standard conditions. Your lab mate suggests that you determine a mixture boiling point by heating the solution (at constant pressure) and then noting the temperature at which it completely changes from all liquid to all vapor. What is wrong with your lab mate's analysis? Why?

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2. The change in molar enthalpy of a particular phase transition at a given T, P is zero. For each of the following, indicate true, false, or there is not enough information to tell.

a) The entropy of phase transition is also zero.

b) A differential increase in P will always will convert the system completely to the phase of higher density, even if T changes differentially also.

c) It is impossible for this system to be single-component.

Fundamentals problems

3. At atmospheric pressure, liquid water expands upon freezing. Explain what this means for the ice-water phase boundary in the P-T plane.

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4. For any phase transition, prove that entropy of the stable phase at lower temperature must be less than that of the entropy of the phase at the higher temperature, along an isobar.

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5. Consider equilibrium between two phases in a single-component system. Show that the change in chemical potential with pressure along the phase boundary is given by:

$$\left(\frac{d\mu}{dP}\right)_{\text{phase boundary}} = \frac{\Delta(1/\hat{s})}{\Delta(1/s)}$$

where $s \equiv S/N$ and $\hat{s} \equiv S/V$.

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6. Consider equilibrium between two phases in a single-component system. Show that the change in chemical potential with temperature along the phase boundary is given by:

$$\left(\frac{d\mu}{dT}\right)_{\text{phase boundary}} = -\frac{\Delta(\rho s)}{\Delta \rho}$$

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7. Originally, second-order phase transitions were defined as those for which the volumes and entropies did not change as one moved from one phase to another, i.e., $\Delta v = 0$ and $\Delta s = 0$. Show that movements along the phase boundary for such transitions must obey the following so-called Ehrenfest relationships:

$$\left(\frac{dP}{dT}\right)_{\text{phase boundary}} = \frac{\Delta\alpha_P}{\Delta\kappa_T}$$

$$\left(\frac{dP}{dT}\right)_{\text{phase boundary}} = \frac{\Delta c_P}{Tv\Delta\alpha_P}$$

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8. A Mollier diagram gives fluid properties as a function of the molar entropy (x-axis) and molar enthalpy (y-axis). In particular, it is highly useful in process calculations involving steam. Various iso-lines in this kind of diagram trace out paths of constant pressure, temperature, and quality (the fraction of vapor versus liquid in the two-phase region).

a) Find an expression for the slope of an isotherm in a Mollier diagram in terms of measurable quantities, in the single phase region. Then, find an expression for the slope of an isobar.

b) What is the functional relationship $H = f(S)$ for an ideal gas along an isobar, assuming a temperature-independent heat capacity? Assume the absolute entropy S_0 and enthalpy H_0 are known at some reference temperature T_0. What is the relationship for an isotherm?

c) Where might an isotherm be vertical, i.e., its slope infinite? Name an example.

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9. If interfacial properties contribute to the bulk thermodynamic behavior of a system, the fundamental equation must be modified to include their effects. Generally, one can write for a single-component single-phase system:

$$dG = -SdT + VdP + \mu dN + \gamma d\alpha$$

where α is the surface area of the system and γ is the surface tension. Note that γ is defined by the change in Gibbs free energy with area at constant T, P, N. Generally, the surface tension is positive, which drives systems towards the minimization of interfacial areas by way of minimizing the Gibbs free energy.

a) Show that the entropy of the system is independent of its area if the surface tension is constant with temperature.

b) If the area is extensive (e.g., scales linearly with N), show that, $(\partial\mu/\partial\gamma)_{T,P} = -\alpha/N$

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10. Consider the system described in the previous problem to be a single-component spherical droplet of radius R in a vacuum, neglecting the possibility of evaporation.

a) Write an expression for the differential Helmholtz free energy of the system. Use this to find an expression relating the equilibrium value of R to the liquid pressure P and surface tension γ, at constant temperature and mole number.

b) Instead of existing in a vacuum, the droplet sits inside a vapor phase of the same component that is metastable with respect to the liquid (i.e., in the process of condensing into the droplet). The droplet and vapor are in thermal and mechanical equilibrium, and are held at constant temperature and pressure. For this system, the Gibbs free energy at constant T, P is given by:

$$dG = \mu^L dN^L + \mu^G dN^G + \gamma_{LG} d\alpha$$

where the superscripts L and G denote the liquid droplet and gas phases, respectively. As liquid condenses into the droplet, show that the free energy change with droplet radius is given by,

$$\frac{dG}{dR} = 4\pi\left(\frac{\Delta\mu R^2}{v} + 2\gamma_{LG}R\right)$$

where $\Delta\mu = \mu^L - \mu^G$ and v is the liquid molar volume (approximately constant).

c) What are the signs of each of the two terms in the expression for dG/dR? Which term dominates at small and large R, respectively? Sketch $G(R)$, the free energy as a function of droplet radius, setting $G(R = 0) = 0$. What is the size of the droplet at the free energy barrier? This approach might be used to find a critical nucleus size and to determine the kinetics of nucleation.

Applied problems

11. The saturation pressure for vapor-liquid equilibria for a given species is fitted to the Antoine equation, $\ln(P_{\text{sat}}/P_{\text{ref}}) = A - B/(T + C)$ where $A, B,$ and C are material-specific constants. Assume the vapor obeys the equation of state $P = Nk_BT/(V - Nb)$ where b is another constant that modifies the ideal gas expression to account for molecular volume.

a) Write an expression for the enthalpy of vaporization as a function of temperature.

b) For water, $P_{\text{ref}} = 1$ kPa, $A = 16.3872$, $B = 3885.70$ K, $C = -42.980$ K, and $b \approx 3.05 \times 10^{-5}$ m^3/mol. How does your estimate of $\Delta h_{\text{vap}}(T = 100\ ^\circ\text{C})$ compare to the experimental value of 40.7 kJ/mol? What is the most likely source of error?

12. At high pressures, water can form a number of ice phases differing in crystallographic structure. Using Figure 10.1, rank order liquid water and its ices from lowest to highest density, to the best of your ability.

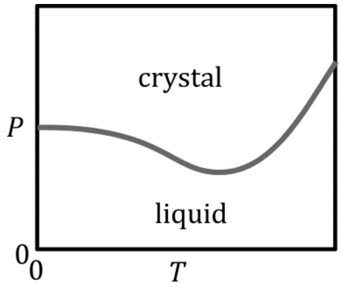

Figure 10.11. Schematic illustration of the solid-liquid phase diagram of the isotope He^3 [adapted from Stillinger, Debenedetti, and Truskett, J. Phys. Chem. B 109, 11809 (2001)].

13. A Kauzmann point is defined as a point in (T, P) space where the entropy difference between two phases equals zero, $\Delta S = 0$. Figure 10.11 gives a schematic phase diagram of the isotope He^3.

a) Indicate any Kauzmann points on this diagram.

b) In general for any substance, consider the locus of all points in the (T, P) plane for which $\Delta S = 0$ between two phases. This will form a line that extends into the metastable regions of the two phases. What is the slope of this line, $(dP/dT)_{\Delta S=0}$, in measurable quantities?

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14. Proteins are biopolymers that can generally exist in two different states: an unfolded state consisting of many unstructured conformations (e.g., the protein "flops" around a lot) and a folded state that is a highly-ordered and stable three-dimensional structure. Typically as one increases the temperature, a protein transitions from folded to unfolded. The quantity that determines which state will be dominant at any one temperature is the Gibbs free energy. In this problem, assume that the heat capacities of each state, $C_{P,\text{folded}}$ and $C_{P,\text{unfolded}}$, are constant.

a) Show that the free energy of folding, $\Delta G_{\text{fold}} = G_{\text{folded}} - G_{\text{unfolded}}$, can be written as

$$\Delta G_{\text{fold}} = \Delta H_{\text{fold},T_f}\left(1 - \frac{T}{T_f}\right) + \Delta C_P\left[T - T_f - T\ln\left(\frac{T}{T_f}\right)\right]$$

where T_f is the folding temperature, i.e., the temperature at which the protein switches from folded to unfolded, $\Delta H_{\text{fold},T_f} = (H_{\text{folded}} - H_{\text{unfolded}})_{T_f}$ is the enthalpy of folding at the folding temperature, and $\Delta C_P = C_{P,\text{folded}} - C_{P,\text{unfolded}}$.

b) The numbers of folded and unfolded proteins in a given solution are proportional to $\exp(G_{\text{folded}}/k_B T)$ and $\exp(G_{\text{unfolded}}/k_B T)$, respectively. Experiments can measure the fraction of proteins that are folded, f, as a function of temperature T. If the heat capacities of the unfolded and folded states are roughly equivalent, how would you estimate $\Delta H_{\text{fold},T_f}$ from such data?