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Lecture 9: Phase Transitions

1 Introduction

Some phases of matter are familiar from everyday experience: solids, liquids and gases. Solid H_2O (ice) melting into liquid H_2O (water) is an example of a phase transition. You may have heard somewhere that there are 4 phases of matter: solid, liquid, gas and plasma. A plasma is an ionized gas, like the sun. I don't know why plasmas get special treatment though – perhaps it's the old idea of the "four elements." In fact, there are thousands of phases. For example, ferromagnetic is a phase, like a permanent iron magnet. When you heat such a magnet to high enough temperature, it undergoes a phase transition and stops being magnetic. Conductors, insulators, and semi-conductors are also phases of matter. At very very high temperatures, nuclei break apart into a quark-gluon phase. Solids generally have lots of phases, determined by crystal structure or topological properties. For example, diamond and graphite are two phases of carbon with different lattice structure:

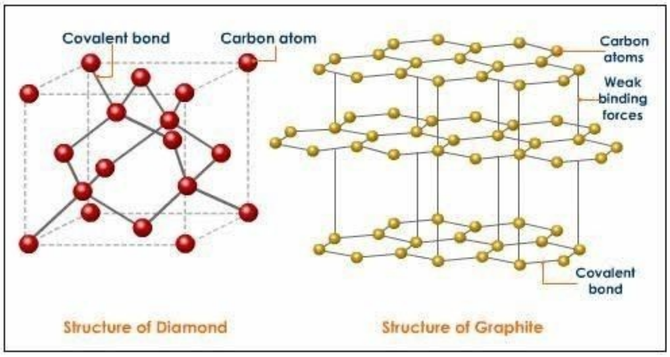

Figure 1. Two of the phases of solid carbon

It's actually quite hard to come up with a precise definition of a phase. Some textbooks say

- A **phase** is a uniform state of matter.

This is an intuitive definition, but not very precise. Taken literally, it is too general: a gas at a different temperature is a different uniform state of matter. So is it a different phase? We don't want it to be. We want "gas" to be the phase.

A more technically precise definition is

- A **phase** is a state of matter whose properties vary smoothly (i.e. it is an analytic function of P, V, T etc).

You might first think that this definition makes liquid H_2O (water) and gasesous H_2O (steam) in the same phase, since we can boil water and it slowly becomes steam. Although this does sound smooth, it is not. For example, consider the temperature of water as heat is added. As you heat it the temperature rises. But when it hits the boiling point, the temperature does not rise anymore, instead the heat goes into vaporizing the water. Then onces it's all gas, its temperature changes again. So the density of H_2O change discontinuously and non-analytically as a function of temperature $\rho(T = 99.9°C)$ is very different from $\rho(T = 100.1°C)$.

Connecting phase to smoothness properties allows to shift focus from phases themselves to the transformations between phases called **phase transitions**. Phase transitions are an incredibly important area of physics.

Physicists take two different approaches to phase transitions. On the one hand, we can treat each phase as its own statistical mechanical system. For example, the ensemble we use to describe ice is very different from the one we use to describe water vapor – neglecting interactions is an excellent approximation for many gases, but a horrible approximation for solids. This makes the discontinuities in density, entropy, etc, across a phase transition inherent in our description. It lets us derive very useful formulas for phase transformations, such as how the pressure and temperature of the phase transformation are related.

The second approach is to construct a statistical mechanical system that describes a substance on both sides of a phase transition. For example, if we knew the exact partition function for N molecules of H_2O, we should be able to see the gas, liquid and solid states arise from different limits. This partition function would necessarily have non-smooth properties across the values of temperature and pressure associated with the phase transition. It is these kinks in otherwise smooth functions that make phase transitions so interesting. Where do they come from? Water itself is too complicated to write down an exact partition function, but there are plenty of simpler systems that we can solve to understand phase transitions. Pursuing these simpler systems leads to concepts you may have heard of like critical phenomena, the renormalization group, mean-field theories, etc. Most of these topics, unfortunately, we will not have time to pursue – phase transitions are the focus of much of modern condensed matter physics and could easily occupy a year-long graduate course.

In this lecture, we will start with discussing the familiar phases of solid, liquid and gas, and understand transitions between them using statistical thermodynamics. Then we will discuss some of the broader, more general aspects of phase transitions.

2 Solids, liquids and gases

It is not hard to figure out what we mean by solid, liquid, or gas. Both solids and liquids are essentially incompressible. The **compressibility** is defined

$$\beta_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T \tag{1}$$

So solids and liquids have $\beta_T \approx 0$. This means no matter how much pressure we put on, we cannot make solids or liquids much denser. Gases have much larger values of β_T. Indeed, from the ideal gas law $PV = Nk_BT$, we see that for a gas $\beta_T = \frac{1}{P} \neq 0$. Compressibility is an example of an **order parameter**, something whose value characterizes the phase.

Solids and liquids of the same substance often have approximately the same density, while the density of gases is much lower. Liquids and solids are called **condensed matter**. Solids differ from liquids and gases in that they are rigid. More precisely, they do not deform under a sheer stress, i.e. they have zero shear modulus S_s. Thus shear stress is an order parmeter for the liquid-solid phase transition. Liquids and gases are collectively called **fluids**.

It may be helpful to say a few more words about liquids. Liquids generally have around the same density as solids, so the atoms are all in contact with each other. Instead of having strong covalent or metallic bonds, like in a solid (cf. Lecture 14), liquids have weaker ionic or hydrogen bonds that keep the molecules close. Although the attractive force in liquids is weak, typical thermal velocities in a liquid are not enough to overcome it.

For example, in water, H_2O, the H-O bonds are covalent, with the shared electrons localized closer to the O than the H. This makes the H slightly positively charged and the O negatively charged. When a two water molecules approach each other, the H from one is then weakly attracted to the O from the other, forming a hydrogen bond. The O in each water molecule can form 2 covalent bonds and 2 hydrogen bonds, giving liquid water a tetrahedral formation. Molecules on the surface of water must have fewer than 2 hydrogen bonds per oxygen, on average. Thus there is any energy cost to having a surface. The Gibbs free energy per area of surface $\gamma = \frac{G}{A}$ is called the **surface tension**:

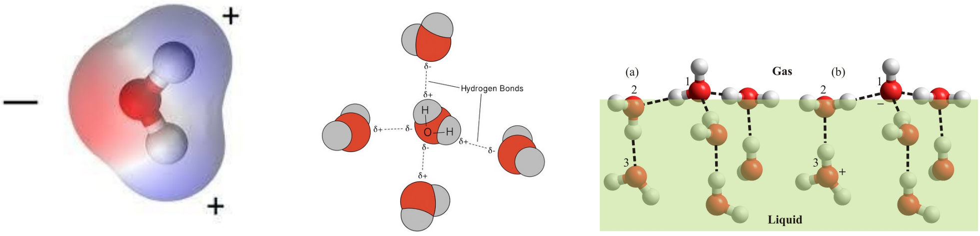

Figure 2. The H and O atoms in water have small charges (left) forming attractive hydrogen bonds (middle). Surfaces cannot saturate all the bonds, therefore there is any energy cost $G = \gamma A$ to having a surface, with γ the surface tension.

All liquids have a surface tension. The surface tension of water happens to be particularly large (e.g. $\gamma_{\text{water}} = 73\frac{\text{mN}}{m}$ compared to say, $\gamma_{\text{CO}_2} = 17\frac{\text{mN}}{m}$), but not the largest (mercury has $\gamma_{\text{Hg}} = 486\frac{\text{mN}}{m}$). One consequence of the surface tension is that a liquid will not expand to fill all the available volume. Liquids form droplets. Even in zero-gravity, water still forms droplets, as does mercury:

Figure 3. (Left) water in zero gravity. (Right) a ball of liquid mercury in zero gravity being hit by a piece of metal.

Whether a solid turns into a liquid when it is heated depends not only on the types of interactions among the molecules, but also on the pressure. At low pressures, when solids are heated, the atoms that break free of their covalent bonds fly off into gas, and the solid sublimates. Only if the pressure is sufficiently high will the molecules stick around close enough to each other for the weak attractive interactions to dominate and the liquid phase to form.

Two phases can be in equilibrium with each other. Consider an unopened bottle of water (constant volume and temperature). The liquid water in the bottle and water vapor in the bottle are in equilibrium. Water molecules are constantly evaporating from the water into the air, and water molecules are condensing into the water at exactly the same rate. Thus volume and temperature are not good ways of characterizing phases. What happens if we open the bottle? Eventually, all the water will evaporate. An open bottle is at constant temperature and pressure. Under these conditions generally a single phase dominates. Thus, phases of matter can be characterized by temperature and pressure.

Why are there single phases at constant T and P? For a single pure substance, the chemical potential is a function of P and T alone: $\mu = \mu(P, T)$. For example, $\mu = k_B T \ln\left(\frac{P}{k_B T \lambda^3}\right)$ for a montatomic ideal gas, where λ is the thermal wavelength, $\lambda = \frac{h}{\sqrt{2\pi m k_B}}$; for a more general ideal gas $\mu = k_B T \ln\left(\frac{P}{k_B T}\zeta\right)$ with ζ the single-particle partition function. There is no N dependence in the chemical potential at fixed P and T since the Gibbs free energy $G(N, P, T) = N\mu$ is extensive.

When there are two phases present the Gibbs free energy is $G = N_1\mu_1(T,P) + N_2\mu_2(T,P)$. Note however one important difference between the two-phase case and the two-chemicals case: when two phases are present there is no entropy of mixing. Solids and liquids coagulate because of the surface tension, so even if multiple phases are present they are always separated and the mixing entropy is tiny if not completely absent (maybe $\Delta S \sim k_B \log(a \text{ few})$ for a few chunks of ice in ice water, but this is negligible compared to the entropies of the ice and water separately $S \sim N k_B$). Another way to see that the mixing entropy is absent is that the pressures are the *same* in two phases; they don't become partial pressures that add up to the total pressure (partial pressure will be relevant of water vapor is mixed with something else, like air, but not for pure water/ice equilibrium that we are discussing here).

At constant temperature and pressure, equilibrium is determined by minimizing the Gibbs free energy G. Recall that

$$dG = V dP - S dT + \mu_1 dN_1 + \mu_2 dN_2 \tag{2}$$

So if ΔN particles go from phase 1 to phase 2 at constant T and P then

$$\Delta G = \mu_1(-\Delta N) + \mu_2(\Delta N) = (\mu_2 - \mu_1)\Delta N \tag{3}$$

Thus, to minimize G, particles move from higher chemical potential to lower chemical potential. This will keep happening until there are no more particles to change phase. Thus at a fixed value of T and P, as long as $\mu_1 \neq \mu_2$, only one phase is allowed. In the law of mass action, the chemical potentials had N dependence which lead to equilibrium situations with different amounts of substances. That N dependence all came from the entropy of mixing. Since here entropy of mixing is absent, one phase completely annihilates the other.

Note that if we express the chemical potential in terms of V rather than P, for a single ideal gas, it takes the form $\mu = k_B T \ln\left(\frac{N}{V}\zeta\right)$. This expression *does* depend on N. So as N changes the chemical potential changes too. Thus, at constant volume, equilibrium can be achieved with finite amounts of two phases. We'll come back to this situation when discussing vapor pressure below.

Returning to constant pressure, it is only when $\mu_1(T,P) = \mu_2(T,P)$ that there is no change in the Gibbs free energy with ΔN, and so only then can the two phases can be present at once. Since $\mu_1(T,P)$ and $\mu_2(T,P)$ are functions, setting them equal generates a curve in the T/P plane. This curve is the **phase boundary**. On the phase boundary two phases are in equilibrium.

A diagram of the phases as a function of pressure and temperature is called a **phase diagram**. Here are some example phase diagrams for carbon dioxide, argon and water.

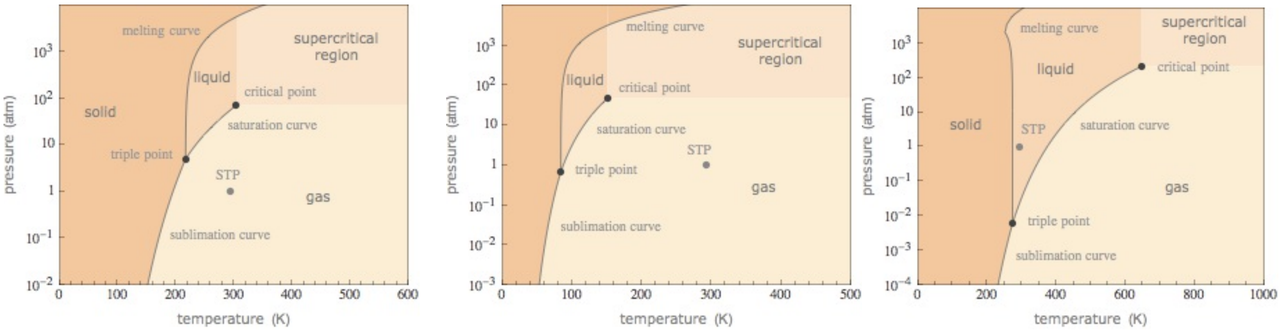

Figure 4. Phase diagrams for CO_2, Ar, and H_2O. The point STP in these plots refers to $T = 20°C = 293K$ and $P = 1$ atm.

The thick lines in the phase diagram are the **phase boundaries**, determined by $\mu_1 = \mu_2$. A **phase transition** is the transformation as a phase boundary is crossed. We define

- **Melting**: transition from solid to liquid.

- **Freezing/Fusion**: transition from liquid to solid.
- **Boiling/vaporization**: transition from liquid to gas.
- **Condensation**: transition from gas to liquid.
- **Sublimation**: transition from solid to gas.
- **Deposition**: transition from gas to solid.

Note in the CO_2 phase diagram that as temperature is increased at $P = 1\,\text{atm}$, CO_2 goes from solid directly to gas: it sublimates. This is why smoke comes off dry ice, but there is no liquid. Liquid CO_2 requires at least 5 atmospheres of pressure.

In a pure phase (off the phase boundary) there is one type of substance and so $G = \mu N$ with N fixed. Then, $\mu = \frac{G}{N}$ and so

$$\left(\frac{\partial\mu}{\partial T}\right)_P = \frac{1}{N}\left(\frac{\partial G}{\partial T}\right)_P = -\frac{S}{N} \tag{4}$$

Since $S > 0$ this implies that the chemical potential always decreases as the temperature goes up. Moreover if there are two phases with different entropies, then as the temperature is raised, the chemical potential of the one with the larger molar entropy (entropy per mole of particles) will go down more. Thus the higher entropy state is preferred at larger temperature. This explains why solids melt when you heat them and liquids boil: the phase transitions are driven by entropy and $S_{\text{solid}} < S_{\text{liquid}} < S_{\text{gas}}$. To be fair, we haven't shown that $S_{\text{solid}} < S_{\text{liquid}} < S_{\text{gas}}$, instead, we can deduce it from phase diagram since when heated solids melt and liquids vaporize.

The first derivative of G with respect to temperature is discontinuous across a phase boundary: infinitesimally below it $\left(\frac{\partial G}{\partial T}\right)_P = -S_{\text{liquid}}$ and infinitesimally above it $\left(\frac{\partial G}{\partial T}\right)_P = -S_{\text{gas}}$. In a pure phase, G is a smooth function (it and all its derivatives are continuous). Therefore, G changes non-smoothly, the phase changes. We'll come back to this in Section 4.

Let's observe some features of the CO_2 phase diagram. First note that liquid/solid phase boundary and the liquid/gas phase boundary intersect. The point where they intersect is a special value of P, T called the **triple point**. At the triple point, three phases are in equilibrium together: $\mu_{\text{solid}} = \mu_{\text{liquid}} = \mu_{\text{gas}}$.

Note also that the phase boundaries do not extend up forever. They end at a point in P, T space called the **critical point**. Critical points are super interesting experimentally and theoretically. An implication of the phase boundary ending is that one can go around the phase transition line. That is, one can smoothly transform a liquid into a gas, without crossing a phase boundary. This is one reason why it is hard to give precise definitions of phases. For example, we said that solids and liquids have small compressibilities β_T. But we didn't say how small. As you move around the critical point from the liquid side, the compressibility gets larger. At some point we don't consider it small and the phase is somewhere between a liquid and a gas – like a very dense gas. So let's not even try to give precise general definitions to different phases. Instead, we'll study transitions between phases. These transitions *are* precisely defined since the phase boundary is precise.

3 Phase boundaries

Suppose we are close to a phase boundary, but on one side of it. Then a single phase completely dominates, and N is fixed ($dN = 0$). Since $\frac{G}{N} = \mu$, then $dG = N d\mu$ and from Eq. (2), $dG = V dP - S dT$, we find

$$d\mu = \frac{V}{N} dP - \frac{S}{N} dT \tag{5}$$

Note the consistency with Eq. (4) at constant P. This holds in any pure phase region, even arbitrarily close to the phase boundary. In particular, it holds on both sides of the phase boundary, as we approach the phase boundary. But on the phase boundary, $\mu_1 = \mu_2$, so the way pressure and temperature must change as we move along the phase boundary is determined by setting $d\mu_1 = d\mu_2$ which gives

$$\frac{V_1}{N_1} dP - \frac{S_1}{N_1} dT = \frac{V_2}{N_2} dP - \frac{S_2}{N_2} dT \tag{6}$$

That is

$$\frac{dP}{dT} = \frac{\Delta\left(\frac{S}{N}\right)}{\Delta\left(\frac{V}{N}\right)} \tag{7}$$

This equation, called the **Clapeyron equation**, determines the shape of the phase boundary.

3.1 Latent heat

The Clapeyron equation involves the change in the molar entropy, $\frac{S}{N}$. Recall that $G = H - TS$ so $\mu = \frac{G}{N} = \frac{H}{N} - T\frac{S}{N}$. Since $\mu_1 = \mu_2$ in equilibrium then $T\Delta\left(\frac{S}{N}\right) = \Delta\left(\frac{H}{N}\right)$ at the phase boundary. So we can can also write the Clapeyron equation as

$$\frac{dP}{dT} = \frac{1}{T} \frac{L}{\Delta\left(\frac{1}{n}\right)} \tag{8}$$

where $n = \frac{N}{V}$ is the number density and

$$L = \Delta\left(\frac{H}{N}\right) \tag{9}$$

is called the **latent heat**.

Latent heat is the change in enthalpy per molecule, like a reaction enthalpy, $\Delta_r H$ but for a phase transition at **saturation** (on the phase transition boundary). It is a heat because as you heat something at saturation, the heat put in changes the entropy by $\Delta S = \frac{Q}{T}$. Since $\Delta S = \frac{\Delta H}{T}$ we have simply that $Q = \Delta H$: the heat put in is the change in enthalpy. The latent heat is the heat put in per molecule to change the phase.

For example, when you boil water, you put more and more heat in, and more water evaporates, but the temperature doesn't change. The heat you put in is providing the energy it takes to break up the hydrogen bonds in the water. The enthalpy of formation of liquid water is $\Delta_f^\circ H = -286\frac{\text{kJ}}{\text{mol}}$ and for water vapor is $\Delta_f^\circ H = -242\frac{\text{kJ}}{\text{mol}}$. The difference between these is the latent heat of vaporization of water at 1 atm: $L_{\text{vap}} = 44\frac{\text{kJ}}{\text{mol}}$. This is positive since it takes heat to boil water. Note that $44\frac{\text{kJ}}{\text{mol}}$ is a large number: water has a lot of energy stored in its hydrogen bonds and it is hard to separate them. For comparison, consider the heat capacity of liquid water $C_P = 75\frac{J}{\text{mol}\, K}$, which implies that to heat water from $0°C$ up to $100°C$ takes only $\Delta H = 7.5\frac{\text{kJ}}{\text{mol}}$ of energy. That is, it takes 6 times as much energy to vaporize water as it does to heat it up to its boiling point from its freezing point: water does not want to evaporate.

That the latent heat of vaporization of water is so large is the reason that sweating is such an efficient form of cooling. Say it's $105°F$ outside, which is higher than body temperature. If you didn't sweat, your body would just heat up until it reached equilibrium with the air. Instead, liquid water forms on your skin, and it draws heat from your body, evaporating into air and cooling your body at the same time. Air conditioners exploit the latent heat of vaporization as well, as we will explore on a problem set. Note that latent heat, which exploits the different chemical potential for different phases, allows temperature differences to *increase* spontaneously. This is not in conflict with the second law of thermodynamics because the total entropy is increasing: the evaporated water has a much larger entropy increase than the entropy decrease from cooling your body.

It's also worth pointing out, for completeness, that the latent heat of fusion for melting ice is $L_{\text{fuse}} = 6.0\,\frac{\text{kJ}}{\text{mol}}$, which is not particularly large. Indeed, it is a much smaller energy than L_{vap}. Note that $L_{\text{fuse}} > 0$ since it takes heat to melt ice.

Using the Clapeyron equation, we can deduce some simple features of phase boundaries. Consider first the solid to liquid transition (i.e. melting). This involves breaking covalent bonds, so $L_{\text{fuse}} > 0$.[1] In general, the density change in going from solid to liquid is usually very small and slightly negative: most solids are slightly more dense than their liquid forms. So $\Delta\left(\frac{1}{n}\right) \gtrsim 0$. Therefore by Eq. (8), $\frac{dP}{dT}$ is generally very large and positive. That is, the liquid/solid phase boundary is usually quite steep and goes slightly to the right in the T/P plane. This can be clearly seen in the phase diagrams in Fig. 4 above.

A well known exception to the density decreasing on melting is water. Water expands when it freezes due to the unusual importance of hydrogen bonding in the liquid. We can see this in the phase diagram in Fig. 4, or more clearly if we zoom in with a logarithmic T axis:

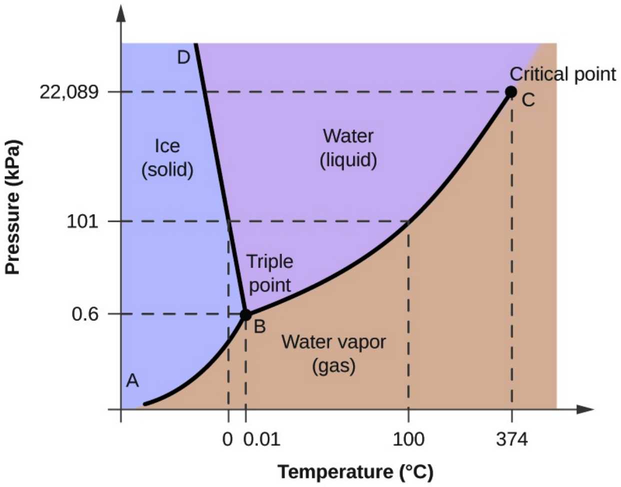

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Figure 5. Phase diagram for water.

Note that the solid liquid boundary goes up and to the left, so $\frac{dP}{dT} < 0$. Since $L > 0$ and $T > 0$ this must mean $\Delta\left(\frac{1}{n}\right) < 0$, as is indeed the case for water. It is the tetrahedral structure of solid ice that makes it not particularly dense. Some other materials with tetrahedral structure (like silicon or gallium) also have denser liquids than solids.

For the transition between liquid and gas (vaporization), the enthalpy change is again positive $\Delta H > 0$, so $L > 0$. In water this is because hydrogen bonds are broken. In general it's because there are attractive interactions among molecules in liquids sticking them together, and it takes energy to separate molecules that are attracted to each other. In addition $\Delta(\text{PV}) = RT$ upon vaporization which also contributes to the latent heat. Gases are usually much less dense than liquids, so $\Delta\left(\frac{1}{n}\right)$ is positive and generally much larger than for the solid-liquid transition. Since the gas density is much less than the liquid density $n_{\text{gas}} \ll n_{\text{liquid}}$, we can write

$$\Delta\frac{1}{n} = \frac{1}{n_{\text{gas}}} - \frac{1}{n_{\text{liquid}}} \approx \frac{1}{n_{\text{gas}}} = \frac{V_{\text{gas}}}{N_{\text{gas}}} = \frac{k_B T}{P} \tag{10}$$

where the ideal gas law $PV = Nk_B T$ was used in the last step. It is conventional to use molar units for latent heat (L is in $\frac{\text{kJ}}{\text{mol}}$), so we replace k_B with the ideal case constant and have

$$\frac{dP}{dT} = \frac{PL}{RT^2} \tag{11}$$

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[1] The only exception is helium. In a small region of the ^{3}He phase diagram, liquid helium solidifies upon heating and $L_{\text{fus}} < 0$.

This is known as the **Clausius Clapeyron** equation. Here L is the **latent heat of vaporization**. The pressure at the liquid-gas transition is called the **vapor pressure**.

Since the latent heat is dominated by the enthalpy change of breaking bonds, we expect it to be a slowly varying function of temperature. If we assume L is independent of T, then we can integrate the Clausius-Clapeyron equation. Writing it as

$$\frac{1}{P}dP=\frac{L}{RT^2}dT \tag{12}$$

we can integrate both sides to give

$$P=C\times\exp\left[-\frac{L}{RT}\right] \tag{13}$$

with C an integration constant. Starting at any point $P=P^\circ$ and $T=T^\circ$ as a boundary condition we then have

$$P=P^\circ\exp\left[-\frac{L}{R}\left(\frac{1}{T}-\frac{1}{T^\circ}\right)\right] \tag{14}$$

For example, at sea level ($P^\circ=1$ bar) water boils at $T^\circ=373\ K$. At 1000 m, the atmospheric pressure is $P=0.9$ bar. Using the latent heat of vaporization of water is $L=42\frac{\mathrm{kJ}}{\mathrm{mol}}$ and $R=8.3\frac{J}{\mathrm{mol}}$, we get

$$T=\left(\frac{1}{T^\circ}-\frac{R}{L}\ln\frac{P}{P^\circ}\right)^{-1}=370.1K \tag{15}$$

which is three degrees lower.

Keep in mind that you cannot extrapolate the Clausius-Clapeyron equation too far. Eventually, the temperature dependence of the latent heat becomes important. For small changes in T and P it is usually makes predictions in excellent agreement with observation.

3.2 Vapor pressure

The **vapor pressure** is the pressure of a pure substance at saturation (on the phase boundary). Generally, vapor pressure refers to the pressure of a gas (vapor), so we use vapor pressure to describe liquid-gas and solid-gas phase transitions. At saturation, two phases can exist in equilibrium. Conversely, if two phases are in equilibrium, the pressure of the gas must be the vapor pressure at that temperature. When there is a mixture of liquids or gases, the partial pressure of each must equal the appropriate vapor pressure in equilibrium.

For example, if we have a sealed bottle of water, there will be some water vapor in the bottle, above the water. If there is only water vapor (no air), then the vapor pressure at room temperature can be determined from the Clausius-Clapeyron equation. Using Eq. (14) at the boiling point $T^\circ=373K$, $P^\circ=1$ atm and $L=42\frac{\mathrm{kJ}}{\mathrm{mol}}$, we find that at room temperature, $T=298K$ that $P=0.034\,\mathrm{atm}=3.142\mathrm{kPa}$. This is consistent with Fig. 5. Note that our calculation implies that the vapor pressure of water at room temperature is much lower than atmospheric pressure. This may seem unintuitive, since it implies that water should not evaporate. Indeed, it would not, if there were no air. In fact, air is only around 1% water at sea level, so the partial pressure of water in air is 0.01 atm which is about 3 times smaller than the vapor pressure. So water does evaporate into air. If you seal a bottle of water at room temperature, the water will start to evaporate and the partial pressure of water in the bottle will increase. It will go up from 0.01 atm to 0.03 atm and then stop, since it matches the vapor pressure. At this point, the total pressure inside the bottle has gone up from 1 atm to 1.02 atm. This small pressure increase is responsible for the pfft you sometimes hear when opening a bottle of water, even if it's not carbonated.

What happens if we mix some solute into the water? For example, how does the vapor pressure of water change when salt is added, and how does its boiling point T_{boil} change? To an excellent approximation, the salt stays in the water, so that only the water is in equilibrium with its vapor. Let $\mu_w(P,T)$ be the chemical potential of pure liquid water, $\mu_{\text{gas}}(P,T)$ be the chemical potential of the pure water vapor, and $\mu_w^{\text{mixed}}(P,T)$ be the chemical potential of water in the saltwater mix. The boiling point $T_{\text{boil}}=T_0$ for pure water at a vapor pressure P_0 satisfies

$$\mu_w(P_0,T_0)=\mu_{\text{gas}}(P_0,T_0) \tag{16}$$

For saltwater, the equilibrium condition is $\mu_w^{\text{mixed}}(P,T)=\mu_{\text{gas}}(P,T)$.

Recall from the discussion of osmotic pressure that the saltwater has higher entropy than pure water, due to entropy of mixing, so it has lower Gibbs free energy, $G=G_0-TS_{\text{mix}}$ and therefore lower chemical potential. For small solute concentrations, we found

$$\mu_w^{\text{mix}}(P,T)=\mu_w(P,T)-k_BT\frac{N_s}{N_w} \tag{17}$$

where N_s is the number of salt molecules and N_w the number of water molecules.

We first ask how the vapor pressure changes at fixed temperature $T=T_0$. Expanding around P_0 by writing $P=P_0+\Delta P$ we get

$$\mu_w^{\text{mixed}}(P,T_0)=\mu_w(P_0+\Delta P,T_0)-k_BT_0\frac{N_s}{N_w}=\mu_w(P_0,T_0)+\Delta P\left(\frac{\partial\mu_w}{\partial P}\right)_T-k_BT_0\frac{N_s}{N_w} \tag{18}$$

Similarly,

$$\mu_{\text{gas}}(P,T_0)=\mu_{\text{gas}}(P_0,T_0)+\Delta P\left(\frac{\partial\mu_{\text{gas}}}{\partial P}\right)_T \tag{19}$$

Now, $\left(\frac{\partial\mu}{\partial P}\right)_T=\frac{V}{N}$ so setting $\mu_w^{\text{mixed}}(P,T_0)=\mu_{\text{gas}}(P,T_0)$ and using Eq. (16) we get

$$\Delta P\left(\frac{V_w}{N_w}-\frac{V_{\text{gas}}}{N_{\text{gas}}}\right)=k_BT_0\frac{N_s}{N_w} \tag{20}$$

The molar volume of the liquid is much lower than the gas (the gas density $n=\frac{N}{V}$ is much larger), so we can drop $\frac{V_w}{N_w}$ compared to $\frac{V_{\text{gas}}}{N_{\text{gas}}}$. Using the ideal gas law, $\frac{V_{\text{gas}}}{N_{\text{gas}}}=\frac{k_BT_0}{P_0}$ we then have

$$(P-P_0)\left(-\frac{k_BT_0}{P_0}\right)=k_BT_0\frac{N_s}{N_w} \tag{21}$$

or

$$\boxed{\Delta P=-\frac{N_s}{N_w}P_0} \tag{22}$$

This is known as **Raoult's law**. It says the vapor pressure decreases when a solute is added proportional to the molar fraction of the solute.

The decrease in vapor pressure can be understood physically. When there is pure water and pure water vapor, there is an equilibrium between molecules evaporating from the solution and condensing into it. When solvent is added, the number density of water on the surface goes down slightly, so fewer water molecules evaporate per unit time while the same number are condensing. Since more condense than evaporate, the gas pressure goes down until equilibrium is reestablished, at a lower vapor pressure.

Knowing how the pressure changes, we can then find the temperature change from the Clausius-Clapeyron equation $\frac{dP}{dT}=\frac{PL}{RT^2}$, Eq. (11). Recall that $\frac{dP}{dT}$ is the slope of the phase boundary. For small ΔP and ΔT we can use $\frac{dP}{dT}=\frac{\Delta P}{\Delta T}$. We want to move back by $-\Delta P$ to restore the original pressure, so

$$\Delta T=-\Delta P\frac{RT^2}{P_0L}=\frac{N_s}{N_w}\frac{RT_0^2}{L} \tag{23}$$

Since $\Delta P<0$ at fixed T, the boundary shifts down/right, thus $\Delta T>0$ at fixed P. The signs of these equations are easiest to undrestand by looking at the liquid-vapor boundary in Fig. 5. A version of this diagram with salt-water included is shown in Fig. 6.

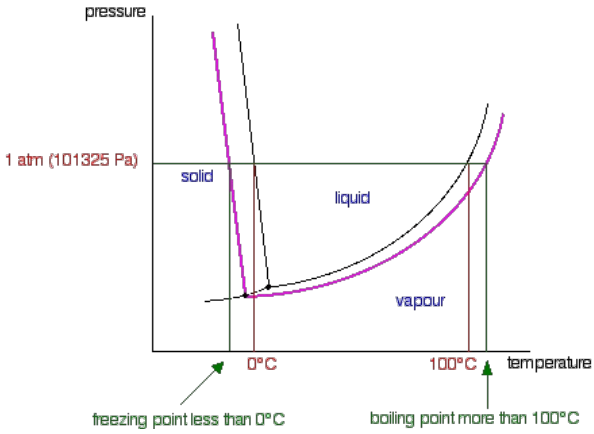

Figure 6. Black curve is the phase boundary for pure water, pink is for salt water. So at 1 atm, the boiling point goes up and the freezing point goes down.

For example, if you add a tablespoon of salt (0.547 mol) to 2 liters of water (111 mol), the vapor pressure at $T=373K$ goes down from 1 bar by $\Delta P=-0.005\,\text{bar}$. Using the latent heat of vaporization of water $L=42\frac{\text{kJ}}{\text{mol}}$ we get that $\Delta T=0.14K$. So the boiling point goes up, but by less than a degree. Thus raising the temperature is not the reason we add salt to water when cooking!

Adding salt to water also lowers its freezing point. The formula is the same as Eq. (23) with the opposite sign, since the salt is in the water, not the ice.[2] See also Fig. 6. Say we put 1 cup of salt (8.7 moles) out per square meter of ice that is 1 mm thick ($1L$ total, 55 moles). The latent heat of fusion for water is $L=6.0\frac{\text{kJ}}{\text{mol}}$, about $1/7^{\text{th}}$ of the latent heat of vaporization. Then

$$\Delta T=-\frac{8.7}{55}\frac{8.3\frac{J}{\text{mol}\,K}(273K)^2}{6.0\,\frac{\text{kJ}}{\text{mol}}}=-16K \tag{24}$$

Thus if you salt your sidewalk, it won't freeze until the temperature drops to $T=-16°C=3°F$.

So salt raises the boiling point and lowers the freezing point. The easiest way to understand this is that the salt disolves in the liquid phase of water. This increases the entropy of the liquid, but not the gas or solid. So it lowers the Gibbs free energy of the liquid relative to the other phases, and makes the liquid relatively preferable.

3.3 Chemical potential phase diagrams

As we saw, phase boundaries are determined by the condition that the chemical potentials of the two phases agree. If we are off a phase boundary, the phase with the lower chemical potential will dominate. To see this, recall that $G=\mu N$ so we are just minimizing Gibbs free energy to find the dominant phase. So at a given pressure, a given phase will dominate over the range of temperatures for which its chemical potential is lowest. This gives us a different perspective on phase transitions which is sometimes useful.

We know that solids will dominate at low temperature and gases at high temperature. Thus the solid phase has the lowest chemical potential at $T=0$ and gas has the lowest chemical potential at high T. We also know that

$$\left(\frac{\partial\mu}{\partial T}\right)_P=-\frac{S}{N}<0 \tag{25}$$

So the slopes of the chemical potential curves at constant pressure are always negative. Moreover, since $S_{\text{solid}}<S_{\text{liquid}}<S_{\text{gas}}$, the gas has the steepest chemical potential curve, followed by liquid, then solid. Finally, since since the entropy of a solid at $T=0$ is zero or nearly zero by the 3rd law of thermodynamics, the solid line starts off horizontal. So a μ/T diagram will look something like this:

---

[2] This shouldn't be obvious, since we used $n_{\text{gas}}\ll n_{\text{liquid}}$, while we can't use $n_{\text{solid}}\ll n_{\text{liquid}}$. We actually used this limit twice: once to drop a term in Eq. (20) and once in Eq. (10). To derive Eq. (23) directly, you can avoid both expansions. Try it yourself!

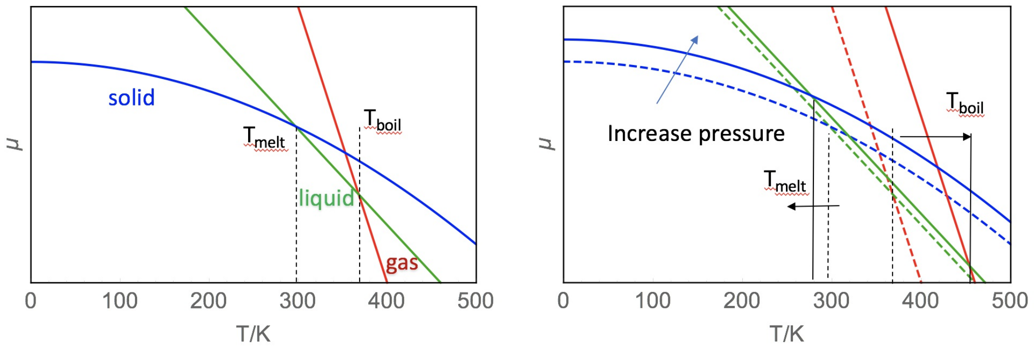

Figure 7. Phase diagram in the chemical potential/temperature plane for H_2O. Left shows the curves at some pressure P. Right shows the effect of increasing the pressure, whereby the dashed lines move to the solid lines.

What happens when we change the pressure? At a given temperature, if we change the pressure then

$$\left(\frac{\partial\mu}{\partial P}\right)_T = \frac{V}{N} = \frac{1}{n} > 0 \tag{26}$$

So the less dense the phase, the more its chemical potential changes, and increasing the pressure always drives the chemical potential up. Thus the gas curve shifts up the most as pressure increases. For water, as shown in the figure, the liquid is denser than the solid so its chemical potential changes less. We see therefore that at higher pressure, the melting temperature for water is lower and the boiling temperature is higher. The increase in temperature of boiling at higher pressure in qualitative agreement with Eq. (14).

Here's another example

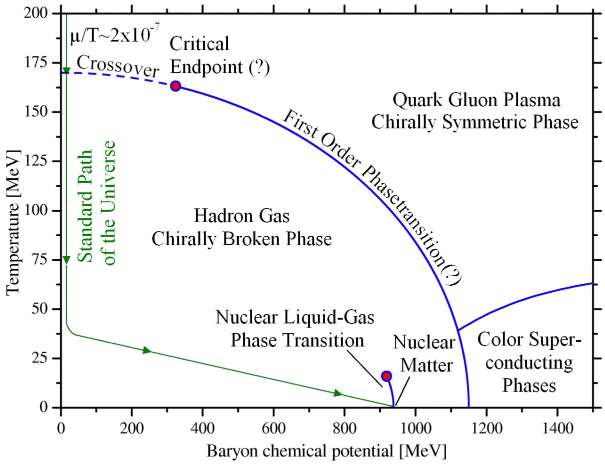

Figure 8. Phase diagram for subatomic matter

This figure shows the phase diagram for subatomic matter: quarks and gluons, as a function of temperature and baryon chemical potential. Baryon chemical potential is the chemical potential for quarks; since quark number is conserved, it can be nonzero. Some information about this phase diagram we know from nuclear physics, some from astrophysics (e.g. neutron stars), some from collisions of ionized lead and ionized gold at particle accelerators, some from cosmology, some from theoretical calculations and simulations. We even have some insight into this phase diagram from string theory. A lot is still unknown. An open question about this phase diagram is whether there is a critical point between the quark-gluon plasma phase and the hadron gas phase (the red dot). This could have implications for the earliest moments of the universe, just after the big bang.

4 General phase transitions

We saw with the liquid/solid/gas phase transitions that $\left(\frac{\partial G}{\partial T}\right)_P$ changes discontinuously at the phase boundary. When this happens we say the transition is of the first order.

- **First-order phase transition**: $\left(\frac{\partial G}{\partial T}\right)_P$ changes discontinuously at the phase boundary

The "first" in "first order" refers to the first derivative of G. It is possible for $\left(\frac{\partial G}{\partial T}\right)_P$ to be continuous, but higher derivatives of G to be discontinuous:

- **nth order phase transition**: $\left(\frac{\partial^n G}{\partial T^n}\right)_P$ changes discontinuously at the phase boundary

This classification of phase transitions is known as the **Ehrenfest classification**. It is common to call any transition with $n > 1$ a **second order transition**. So in common parlance

- **Second-order phase transition**: $\left(\frac{\partial G}{\partial T}\right)_P$ is continuous across the phase boundary

This is because first order transitions are special: they have latent heat, which is a barrier to changing phases. Second order transitions are smooth and have no barrier. They occur at points in phase diagrams where the phases merge into one, and the latent heat vanishes.

In modern treatments, we use first and second order a little more loosely. It doesn't have to be the Gibbs free energy that determines the order, it can be the Helmholtz free energy, or just the energy, depending on what is appropriate for the problem. And it doesn't have to be derivative with respect to temperature, but can be some other derivative of the energy. The thing whose continuity we are questioning is called the **order parameter**. For example, in the Ehrenfest classification, the entropy $S = -\left(\frac{\partial G}{\partial T}\right)_P$ is the order parameter. For boiling water, density is a natural order parameter and a little more intuitive than the entropy. At fixed N and m the density $\rho = \frac{Nm}{V}$ is equivalent to using $V = \left(\frac{\partial F}{\partial P}\right)_T$.

4.1 Paramagnetism

Paramagnetic means that a material is attracted to an applied magnetic field, like iron filings to a magnet. Many elements (gold, potassium, calcium,...) are paramagnetic. Most compounds and stable molecules are weakly paramagnetic. Paramagnetic materials generally have unpaired electrons that are free to align the external field, while diamagnetic materials have closed orbits. The opposite of paramagnetic is **diamagnetic**, which means something is repelled by an applied magnetic field (google "levitating frog" for example). A third type of magnetism is **ferromagnetism**, whereby a material can produce a coherent magnetic field, i.e. as in an ordinary iron refrigerator magnet. If you heat an iron magnet above 1043 K it will lose its magnetism and become paramagnetic. The transition between paramagnetic and ferromagnetic phases of iron is an example of a phase transition.

The ferromagnetism in iron comes about when all the magnetic spins in iron are aligned. The spins themselves can be thought of as little magnets that attract each other.

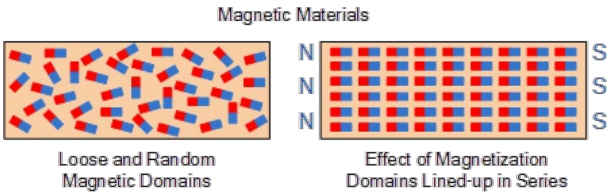

Figure 9. When a magnetic material is cooled, its spins spontaneously align as it enters the ferromagnetic phase.

In this crude model, each pair has energy $-\varepsilon$ if they are aligned and $+\varepsilon$ if they are not aligned. So the difference between the fully aligned (ferromagnetic) state and disordered (paramagnetic) state is roughly $E = 2N\varepsilon$. On the other hand, the disordered state has much higher entropy. The entropy of the fully-aligned magnetic state is zero. But the disordered state has $\Omega = 2^N$ configurations and entropy $S = Nk_B \ln 2$. Thus the free energy in the magnetic state is

$$F_{\text{magentic}} = E - TS = -N\varepsilon \tag{27}$$

and the free energy of the disordered state is

$$F_{\text{disordered}} = E - TS = N(\varepsilon - Tk_B \ln 2) \tag{28}$$

By minimizing the free energy we see that the transition from paramagnetic to ferromagnetic state occurs when these free energies cross each other, which is at

$$k_B T_c \approx \frac{2\varepsilon}{\ln 2} \tag{29}$$

T_c is known as the **Curie temperature**.

What is a good order parameter for the transition? Entropy S should work, as it goes from $S = Nk_B \text{ln}2$ down to zero. Unlike the liquid/gas transition however, the entropy change as the magnet is cooled will be smooth: at temperatures near T_c the magnetic will have some spins aligned, be slightly ferromagnetic and have some intermediate entropy. Thus the ferromagnetic phase transition is second order.

Another order parameter we could consider is the magnetization M. The direction of the magnetic field is a vector $\overrightarrow{M}$, and we can define $M = |\overrightarrow{M}|$. Above T_c, $M = 0$ exactly. As T is lowered, M is nonzero. This function $M(T)$ is going to be continuous across T_c. However all of the derivatives of $M(T)$ cannot be continuous – if they were then the function would have to be $M(T) = 0$ exactly for all T (mathematically, this is a property of analytic functions).

It is interesting to think of the direction of $\overrightarrow{M}$ rather than its magnitude as the order parameter. In the magnetic phase, the direction of $\overrightarrow{M}$ picks up some definite value (there can be domains inside the magnetic with different directions, but let's just focus on one domain for now). One super interesting thing about $\overrightarrow{M}$ picking up a direction is that we cannot know ahead of time which direction it would be. At high temperature no direction is preferred. Indeed, all the spins are constantly flipping around in 3D. So the theory at high temperature is rotationally invariant. At low temperature, it is not. But fundamentally, the interactions between spins are like $\vec{s}_1 \cdot \vec{s}_2$ involving a rotationally-invariant dot product. So the Hamiltonian is rotationally invariant and it is only the state that violates the symmetry. When this happens we say that the rotational symmetry is **spontaneously broken**.

Symmetries are an extraordinarily powerful tool in physics. In this context, they help specify phases and phase transitions. For another example, note that a liquid is invariant under translations. Microscopically, of course the molecules are in particular positions. But knowning the position of some of the molecules does not tell us anything about where molecules far away are. On the other hand, a solid is *not* translationally invariant. Once you know where one atom is, you can pinpoint all the rest throughout the crystal. We say the solid has long-range order. So when a liquid freezes, translational symmetry is spontaneously broken and long-range order results.

There are lots of consequences of spontaneous symmetry breaking. One is that it tells us that there must be arbitrarily low energy excitations of the system. This very general result is known as **Goldstone's theorem**. For example, in a solid, we know we can push it and it will move. It can move arbitrarily slowly, so we can push it with arbitrarily low energy to have an effect. However, as we push it, what we actually do is push the atoms on the side where our hand is. These atoms push the next atoms, and so on, all throughout the solid. So really, to move the solid by pushing, we are setting up a wave of very low energy. As we move an atom, the system works to restore the lattice to how it was. This doesn't happen in a liquid where the translation symmetry is unbroken. The excitations of a solid are called **phonons** and have a massless dispersion relation $\omega(k) \to 0$ as $k \to 0$. Phonons are covered in Lecture 11. The excitations in a magnet from the spontaneously broken rotational symmetry also have $\omega(k) \to 0$ as $k \to 0$. They are called **spin waves**.

To understand spontaneous symmetry breaking, the emergence of long-range order, etc. requires techniques of condensed matter physics that take us well beyond the course material.

4.2 Critical phenomena

The final topic I want to mention concerns that dot at the end of the liquid/gas phase boundary denoted as the **critical point**. Critical points are super-interesting places with a lot of unusual properties.

Recall that as you heat up a liquid, it will eventually vaporize. At the point of the phase transition, the heat will go into latent heat of vaporization and the temperature will not change. Eventually, all the liquid is vaporized and the heat will start raising the temperature again. We can see this fairly clearly in a phase diagram in the pressure-volume plane, as this one for CO_2:

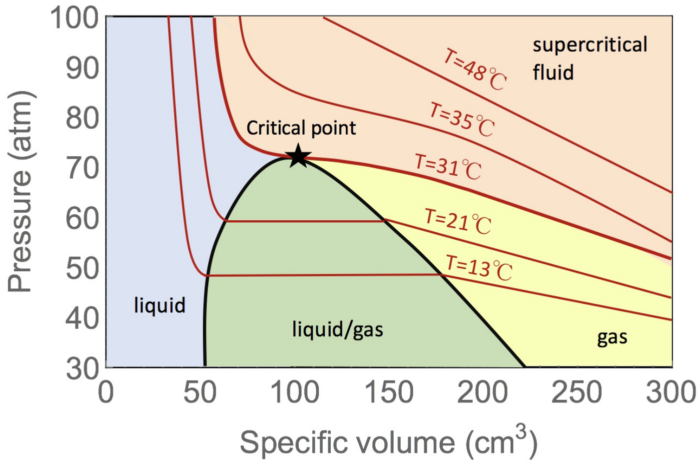

Figure 10. P-V phase diagram for CO_2. The x-axis is the specific volume, $v = \frac{V}{N}$. The green region has liquid and gas.

The lines in this plot are lines of constant temperature, or **isotherms**. Say we start on left in the liquid region, along the $T = 13°C$ isotherm. As we decompress the CO_2 isothermally, we will move along the isotherm, lowering pressure and increasing the specific volume (lowering the density). When we hit the phase boundary, the liquid starts vaporizing. During the phase transition pressure and temperature are fixed, so we move horizontally, $\frac{\partial P}{\partial v} = 0$. After the phase transition is complete, CO_2 is all gas, and the decompression lowers the pressure and density once again. So the isotherm gives a decreasing function $P(v)$ outside of the coexistence region and is flat in the coexistence region.

A natural order parameter for the transition is the number density n, or equivalently the specific volume, $v = \frac{1}{n}$. We see from the figure that the specific volume changes discontinuously from liquid to gas along the $T = 13°C$ isotherm, so the transition at this temperature is 1st order.

Now consider what happens as the temperature is increased. As you can see from the figure, at a higher temperature, the difference in specific volume between the liquid and gas phases at constant temperature is smaller. The latent heat of vaporization is smaller too. Eventually, there is no difference between the liquid and gas phases and the latent heat vanishes: it takes no energy to convert a liquid to a gas. This happens at the critical temperature T_c, which intersects the liquid/gas coexistence region at the critical specific volume v_c and critical pressure P_c, that is, at the critical point. The specific volume changes smoothly from liquid to gas if we pass through the critical point, so the phase transition at this point is second order.

At temperatures above the critical temperature, the material is both gas and liquid, or neither gas nor liquid, depending on how you look at it. We call it a **supercritical fluid**. The "super" in this context just means "beyond" – in contrast to the "super" in superfluids or superconductors which are truly exotic phases of matter. A supercritical fluid is in between a gas or a liquid. For example, supercritical CO_2 is used to decaffeinate coffee – its viscosity and diffusivity are like those of a gas, so it penetrates the beans easily, and its density is like that of a liquid, so a lot of it can get in. It happens also to bind well to caffeine (this property is much more important that its supercritical fluid properties). Supercritical CO_2 is also used in dry cleaning.

On any isotherm in the liquid/gas region, $\left(\frac{\partial P}{\partial v}\right)_T = 0$. At the critical point, the length of the horizontal part of the isotherm has gone to zero, but it is still flat. Moreover, since the isotherms are decreasing on either side of the critical point, we know that $\left(\frac{\partial^2 P}{\partial v^2}\right)_T = 0$ as well: the critical point is a point of inflection. It also happens to be true that, but is not so easy to show, that all of the derivatives of P vanish, $\left(\frac{\partial^n P}{\partial v^n}\right)_T = 0$. Mathematically, this means that $P(v)$ is a non-analytic function at the critical point. Second order phase transitions are super interesting because somehow this crazy mathematical behavior, where all the derivatives vanish, arises out of functions like the entropy S or the partition function Z that depend smoothly on temperature, pressure, volume, etc.

It's not just the derivatives $\left(\frac{\partial^n P}{\partial v^n}\right)_T$ that vanish. We could equally well have looked at the phase diagram in the $T - v$ plane:

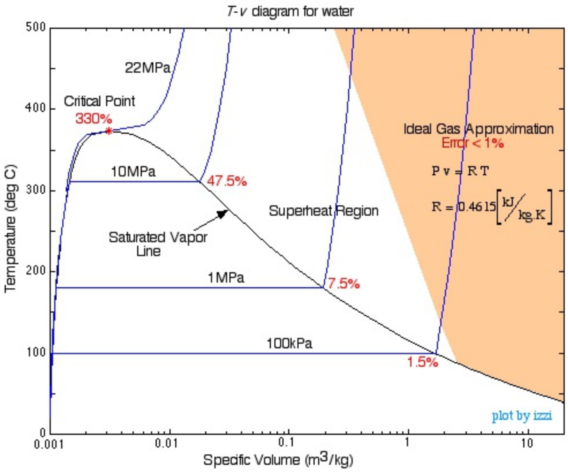

Figure 11. TV diagram for water

In this case, at subcritical pressure, water increases its specific volume when heated until it boils. At the critical point, the latent heat vanishes and the water and steam become the same. The critical point is also a point of inflection for $T(v)$, and in fact, $\left(\frac{\partial^n T}{\partial v^n}\right)_P = 0$, so $T(v)$ is a non-analytic function.

Away from the critical point, the various thermodynamic quantities that we have discussed, latent heat, enthalpy of formation, heat capacity, isothermal compressibility, etc., help us distinguish one material from another. But these are all related to derivatives of thermodynamic quantities. Because all the derivatives vanish, $\left(\frac{\partial^n P}{\partial v^n}\right)_T = \left(\frac{\partial^n T}{\partial v^n}\right)_P = 0$, all the dimensionful physical quantities we use to characterize a material either vanish or are infinite at this point. For example, here is a plot of heat capacity of propane near the critical point:

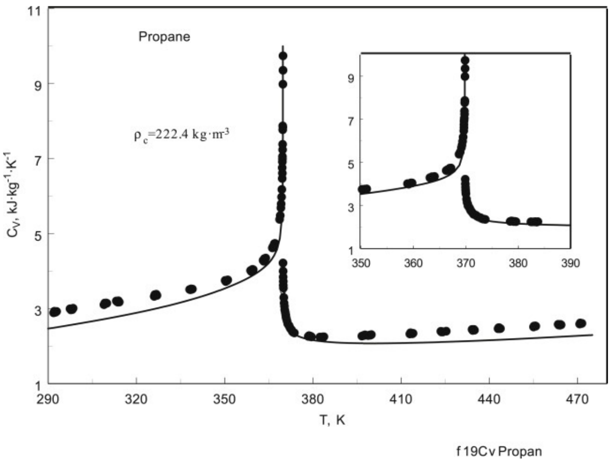

Figure 12. Heat capacity of propane near the critical point, showing the singularity.

One way to understand the disappearance of scale more physically is to think about water. The difference between liquid water and an ideal gas is that water has hydrogen bonds (see Fig. 2). In water vapor, the molecules are generally too far apart for hydrogen bonds to matter. The relative importance of hydrogen bonds in water versus gas determines the surface tension γ and everything else that makes water a liquid. However, as the density or pressure on the gas is increased, the relative importance hydrogen bonds in the vapor phase increases too. Consequently the surface tension of the liquid/gas boundary goes down. So typical droplet sizes grow. At the critical point, the surface tension vanishes and droplets of any size can form: the single dimensional scale (the surface tension γ) has vanished. This can be seen through the phenomenon of critical opalescence.

We say that the theory near the critical point is **scale-invariant** or **conformal**, since no dimensionful quantity is available to characterize the material. That is, choosing units relative to the critical values:

$$\hat{T} = \frac{T}{T_c}, \quad \hat{P} = \frac{P}{P_c}, \quad \hat{v} = \frac{v}{v_c}, \quad \hat{n} = \frac{1}{\hat{v}} = \frac{n}{n_c} = \frac{\rho}{\rho_c} \tag{30}$$

all thermodynamic quantities, such as the free energy, become *independent of any other property of the material*. For example, P_c and T_c for neon, argon, krypton, xenon, N_2, O_2, CO and CH_4 are

	Ne	Ar	Kr	Xe	N_2	O_2	CO	CH_4
$T_c\,(°C)$	-228.7	1122.3	-63.8	16.6	-147	-118.4	-140	-82.1
$P_c\,(\text{atm})$	26.9	48	54.3	58	33.5	50.1	34.5	45.8

(31)

These temperatures and pressures are dimensionful quantities, with no apparent relation among them. Now, we rescale the temperatures, pressures, specific volumes and specific densities by these critical values and look at $\hat{T}$ and $\hat{n}$ near the critical points for the different materials:

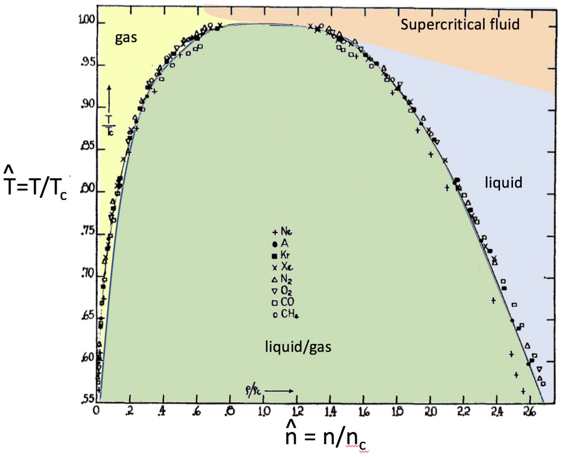

Figure 13. Reduced temperature versus reduced number density for a variety of different substances at saturation. Adapted from E.A. Guggenheim, J. Chem. Phys. 13, 253 (1945).

Remarkably, in the vicinity of the critical point, the $\hat{T} - \hat{n}$ phase boundaries all have exactly the same shape! This implies that all of the derived quantities, such as heat capacity, isothermal compressibility, etc, should be related in every material near its critical point. This powerful observation is known as the **law of corresponding states**.

The shape in Fig. 13 is fit by a functions $\hat{n}(\hat{T})$ on the liquid and gas side of the form

$$\hat{n}_\ell(\hat{T}) = 1 + \frac{3}{4}(1 - \hat{T}) + \frac{7}{4}(1 - \hat{T})^{1/3}, \qquad \hat{n}_g(\hat{T}) = 1 + \frac{3}{4}(1 - \hat{T}) - \frac{7}{4}(1 - \hat{T})^{1/3} \tag{32}$$

The fractional exponent makes these functions non-analytic, so that all the derivatives are singular at the critical point $\hat{T} = 1$, $\hat{n}^{(k)}(1) = \infty$. This means all the derivatives of $\hat{T}(\hat{n})$ vanish at the critical point $\hat{n} = 1$, $\hat{T}^{(k)}(1) = 0$.

The exponent $1/3$ in Eq. (32) is an example of a **critical exponent**. It characterizes the approach of the density towards the critical point. If we used an order parameter other then density, for example, the heat capacity, it would approach the critical point with a different scaling behavior $C_V \sim (1-\hat{T})^{-\alpha}$. Because of the law of corresponding states, the critical exponents can be calculated with any material for which the order parameter applies. In fact, the material can be a made-up theoretical one: the universality is so strong that the material doesn't even have to exist. An important example is the ising model, which treats a material as a lattice of spins with interaction energies taking the values ± 1. Computing the critical exponents of the ising model agrees with measured values of the critical exponents in water to one part in 1000!

5 Summary

This lecture introduced the notion of a phase of matter. Unfortunately, it has hard to define what a phase is precisely, since one often smoothly go between two phases. For example, at very high temperature, liquid water and gaseous water are pretty hard to tell apart. There are two ways out.

First, we can use the term "phase" to partition states of matter only into regions that cannot be smoothly transformed into each other. With this definition, liquid and gaseous water are the same phase, but solid is different. The solid phase has less symmetry than the liquid/gas phase (discrete translational symmetry instead of full continuous translational and rotational symmetry). More generally, one can go further and define phases by their symmetries. This approach can be very powerful and mathematically rigorous. However, it sidesteps the fact that liquid and gaseous water clearly are different!

Second, we can take a more local point of view, and define phases as regions where a particular theoretical model is accurate. The model amounts to a set of assumptions and the specification of a partition function. For example, we could neglect interactions to make an ideal gas. Then the smooth transition between phases goes through a region where the assumptions break down. When two models are accurate in the same thermodynamic region (P, V, T), there is a phase boundary. This is a more general treatment of phases than the first option, but requires approximations. Indeed, the business of physicists is making approximations, and such approximations necessarily break down. This second approach is typically what physicists mean by a phase.

When you have a phase boundary, the chemical potentials/Gibbs free energies of the two phases must agree. Indeed, the equality of chemical potentials is a neccessary condition for equilibrium. However, the entropy, which is the derivative of μ with resect to T, might not be continous. When S changes abrubtly, we say the phase transition is first order. So the chemical potential has a kink for a first order phase transition. If S is continous, but $\frac{\partial S}{\partial T} = \frac{\partial^2 \mu}{\partial T^2}$ is not continous, we say the transition is second order.

Phase boundaries are fascinating places. The slope of the phase boundary is given by the Clausius equation $\frac{dP}{dT} = \frac{1}{T} \frac{L}{\Delta\left(\frac{1}{n}\right)}$, where the latent heat L is the change in (molar) enthalpy between the two phases $L = \Delta\left(\frac{H}{N}\right)$. For liquid-gas transitions, the Clausius equation simplies to the Clausius-Clapyron equation $\frac{dP}{dT} = \frac{PL}{RT^2}$ Latent heat is the energy cost of a phase transition. When you boil water, you break up all the hydrogen bonds to make liquid gas. The latent heat quantifies this. As you move along a phase boundary, the latent heat can get smaller and smaller until it finally vanishes. The vanishing point is called the critical point. The phase transition is first order when $L \neq 0$ and becomes second order when $L = 0$. The latent heat characterizes the energy scale of the phase transition, so when $L = 0$ there is no scale, and so critical points are characterized by long-range correlations.

We are often interested in how phase boundaries change when we modify the phases. For example, adding salt to water changes its boiling point. Studying phase boundaries has allowed us to quantify these effects, through equations like Raoult's law.