General Considerations

• *Setup:* We saw how to find the phase coexistence line in the p-T plane, by integrating the Clausius-Clapeyron equation $\mathrm{d}P_0(T)/\mathrm{d}T = \Delta s/\Delta v$. Now we look at phase transitions in more detail, and in particular see if we can predict under what conditions transitions will occur using the equation of state in the form $p = p(V,T)$. (Notice that phase transitions are very far from the behavior of ideal gases, so we cannot assume that the fluid is close to an ideal gas and use, for example, a virial expansion of the equation of state.)
• *Liquid-gas phenomenology:* If we follow the behavior of a fluid along an isothermal line in the p-V plane, the discontinuity in V at the phase transition is more obvious, and we can also clearly see the difference with respect to an ideal gas [$\star$ plot $\star$]. If we imagine starting with a real fluid in the liquid phase at $T < T_\mathrm{c}$, and lowering p by increasing V isothermally, when p reaches the value $P_0(T)$, some of the fluid starts becoming gas and increases its volume, without lowering p further until all of it is gas. How can we find $P_0(T)$ in terms of the $p(V,T)$ equation of state?

The van der Waals Gas Example

• *Reminder:* We saw that, if b is the excluded volume per particle arising from the short-range repulsion, and a measures the long-range attraction between particles, then the van der Waals equation of state is

$$p = \frac{k_\mathrm{B}T}{v-b} - \frac{a}{v^2}\ .$$

• *Isothermal lines:* Based on this equation of state, for every T and p there are either 1 or 3 possible values of v, the real solutions of a cubic equation. For very high T, the second term on the right is negligible, and there is only one solution, of the modified perfect fluid form $v = k_\mathrm{B}T/V + b$. Two more real solutions appear below some critical isothermal line T_c, at pressure p_c and volume v_c, where $\partial p/\partial v|_T = 0$ and $\partial^2 p/\partial v^2|_T = 0$.
• *The critical point:* To find it, solve the set of equations given by the equation of state and the vanishing of the first two derivatives. One gets that $p_\mathrm{c} = a/27b^2$, $v_\mathrm{c} = 3b$, and $k_\mathrm{B}T_\mathrm{c} = 8a/27b$. If we use these to define dimensionless $\tilde p$, $\tilde v$ and $\tilde T$, we get the universal relation van der Waals called Law of Corresponding States,

$$\tilde p = \frac{8\,\tilde T}{3\,\tilde v - 1} - \frac{3}{\tilde v^2}\ .$$

• *The phase transition:* ...

Types of Phase Transitions

• *Critical points:* The liquid-gas phase transition for a van der Waals gas has a critical point, above which no transition occurs. This is a common feature for liquid-gas transitions, where at high pressures/temperatures the fluid varies smoothly from one phase to the other, but does not occur usually in solid-liquid phase transitions, which involve the establishment of long-range correlations.
• *Order of the phase transition:* In the van der Waals case the volume per particle, an example of quantity obtained as a first derivative of a thermodynamical potential, is discontinuous; the phase transition is first-order. In general, if the lowest derivative of a thermodynamic potential that has a discontinuity is the nth, we have an nth-order phase transition. A discontinuity in κ_T would signal a second-order phase transition.

The Ferromagnet (Ising Model) Example

• *Qualitatively:* In this case, as one finds out from the mean-field approximation and the Monte Carlo simulations, there is a second-order phase transition at which χ is discontinuous.
• *Susceptibility and long-range order:* The susceptibility for a paramagnetic or ferromagnetic material is $\chi(T,B) = \partial\bar M/\partial B = N\mu\,\partial\langle s\rangle/\partial B$.

Relevant Sections: [PHY 731]; Chandler, §2.3 (37-44); Halley; Reif, §8.6; Schwabl, 242-257.
Related Topics: See references related to the metric on the space of states in black hole thermodynamics.