Pre-class Preparation


Wednesday
Read: Chapter 11, Sec. 11.1 (Stable and metastable phases) and 11.2 (Maxwell construction)
Pre-class question: 11.10: What is it unstable to?, and 11.13: Gibbs free energy barrier.
(Submit electronically by 9:30 Tuesday evening.)

Friday
Read: Chapter 11, Sec. 11.3 (Nucleation: critical droplet theory)
Pre-class question: 11.11: Droplet Nucleation in two dimensions. (Submit electronically by 9:30 Thursday evening.)

Monday
Read: Chapter 11, Sec. 11.4 (Morphology of abrupt transitions)
Pre-class question: 11.12: Linear stability of a growing interface. (Submit electronically by 9:30 Sunday evening.)

Exercises

Those in 4488 may choose two of the four exercises.

10.7: Noise and Langevin equations, or (if you did this earlier by accident), 6.18
10.9: Quasiparticle poles and Goldstone’s theorem.
11.5: Nucleation of dislocation pairs.
11.8: Minimizing sequences and microstructure.
11.14: Fracture nucleation: Elastic theory has zero radius of convergence.
In-class exercises

Day 1

10.15 Fluctuation dissipation for the harmonic oscillator.  
This is a continuation of Exercise 10.11, where you derived the correlation function
\[ C_Q(\tau) = A \exp(-\lambda \tau) \]
for the overdamped harmonic oscillator with rate \( \lambda \), and the
correlation function
\[ C_X(\tau) = A \exp(-\lambda \tau) + B \exp(-\Lambda \tau) \]
for the sum \( X = Q + q \) of two uncoupled oscillators with overdamped decay rates \( \lambda \) and \( \Lambda \). In Exercise 10.13 we
calculated the susceptibility directly. Now we shall calculate it using the fluctuation-dissipation theorem.

(a) Using the classical fluctuation-dissipation theorem, eqn 10.60, derive the time-dependent susceptibilities
\[ \chi_Q(\tau) \]
and
\[ \chi_X(\tau) \]. You may leave your answer in terms of \( A \) and \( B \).

(b) Sketch a graph of \( \chi_X(\tau) \) for \(-1/\lambda < \tau < 1/\lambda\), assuming that \( \lambda \approx \Lambda/10 \) and
\( A \approx 2B \).

Day 1

10.17 Kramers–Krönig for the harmonic oscillator.  
In general, susceptibilities are causal: \( \chi(\tau) = 0 \) for \( \tau < 0 \) because the response cannot
precede the force. We saw in general that this implied that \( \tilde{\chi}(\omega) \) had to be analytic in
the upper half plane, \( \text{Im}(\omega) > 0 \).

Let us check this for the overdamped harmonic oscillator, where \( \chi(\tau) = C \exp(-\lambda \tau) \).

What is \( \tilde{\chi}(\omega) \)? Where are its poles? Are they in the upper half plane? Are there any
singularities in the lower half plane? (Beware: The conventions on Fourier transforms
are pretty strange (Appendix 13). Whether the poles are in the upper or lower half
plane depends on whether going from \( t \) to \( \omega \) multiplies by \( \exp(i\omega t) \) or by \( \exp(-i\omega t) \).
Equation A.6 tells us the former choice is correct, but eqn A.9 tells us the opposite
convention holds for spatial Fourier transforms.)

11.1 Maxwell and van der Waals.  
The van der Waals (vdW) equation
\[ (P + N^2a/V^2)(V - Nb) = Nk_B T \]  
(1)
is often applied as an approximate equation of state for real liquids and gases. The term
\( V - Nb \) arises from short-range repulsion between molecules (Exercise 3.5); the term
\( N^2a/V^2 \) incorporates the leading effects2 of long-range attraction between molecules.

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1A printable version of Fig. 1 can be found at the book Web site [2].
2These corrections are to leading orders in the density; they are small for dilute gases.
Fig. 1 P–V plot: van der Waals. Van der Waals (vdW) approximation (eqn 1) to H$_2$O, with $a = 0.55$ J m$^3$/mol$^2$ ($a = 1.52 \times 10^{-35}$ erg cm$^3$/molecule), and $b = 3.04 \times 10^{-5}$ m$^3$/mol ($b = 5.05 \times 10^{-23}$ cm$^3$/molecule), fit to the critical temperature and pressure for water.

Figure 1 shows the pressure versus volume curves for one mole of H$_2$O, within the vdW model. A real piston of water held at constant temperature would in equilibrium pass through three regimes as it expanded – first a decompressing liquid, then coexisting liquid and vapor at constant pressure (as the liquid evaporates or boils to fill the piston), and then a decompressing gas. The Maxwell construction tells us what the vapor pressure and the two densities for the coexisting liquid and gas is at each temperature.

Get a copy of Fig. 1. By hand, roughly implement the Maxwell construction for each curve, and sketch the region in the P–V plane where liquid and gas can coexist.

Day 2

11.2 The van der Waals critical point. (Chemistry)

The top of the coexistence curve in Fig. 1 is the pressure, density, and temperature at which the distinction between liquid and gas disappears. It is the focus of much study, as the prime example of a critical point, with self-similar fluctuations and scaling behavior.

(a) Identify this point on a sketch of Fig. 1. The vdW constants are fit to the critical temperature $T_c = 647.3$ K and pressure $P_c = 22.09$ MPa = $220.9 \times 10^6$ dyne/cm$^2$; check that your estimate for the critical point roughly agrees with the values quoted. I have
found few references that quote the critical volume per mole, and the two I have found disagree; one says around 50 cm$^3$/mol and one says around 55. Plot the true critical point on your sketch. Is the location of the critical density of water predicted well by the vdW equation of state?

Your sketch from Exercise 11.1 may not be precise enough to tell this, but the vdW phase boundaries meet at the critical point with a quadratic maximum: $1/\rho_l - 1/\rho_g \sim (P - P_c)^{1/2}$, where $\rho_l$ and $\rho_g$ are the densities on the coexistence boundary (moles per volume) at the pressure $P$. Indeed, the peak of any ‘mean-field’ prediction like van der Waals, gotten from analytic formulas, will have a Taylor series whose quadratic term gives an exponent 1/2. Similarly, one can show that the vdW equation of state implies that

$$\rho_l - \rho_g \sim (T_c - T)^{1/2} \sim (-t)^{1/2}. \tag{2}$$

(b) Compare this latter prediction with Fig. 12.6(a). What critical exponent $\beta$ does the van der Waals equation predict, assuming eqn 2? How does it compare to the actual value, $\beta = 0.326419\ldots$?

This technical-seeming error in the shape of the maximum of the liquid-gas line was an early puzzle that led eventually to the discovery of self-similarity and universality, and the invention of the renormalization group (Chapter 12).

Day 2

11.3 Interfaces and van der Waals. (Chemistry)

The chemical potential per particle for the vdW equation of state is

$$\mu[\rho] = -k_B T + P/\rho - a\rho + k_B T \log(\lambda^3 \rho) - k_B T \log(1 - b\rho), \tag{3}$$

where $\rho = N/V$ is the density.

(a) Show that $\mu$ is minimized when $\rho$ satisfies the vdW equation of state, eqn 1.

(b) According to the caption to Fig. 2, what is the vdW approximation to the vapor pressure at 373K = 100$^\circ$C? How close is the vdW approximation to the true vapor pressure of water? (Hint: Atmospheric pressure is around one bar = 0.1 MPa = 10$^6$ dynes/cm$^2$. What happens when the vapor pressure hits atmospheric pressure?)

We can view Fig. 2 as a kind of free energy barrier for the formation of a liquid–gas interface. If $\mu_0$ is the common chemical potential shared by the water and the vapor at this temperature, the extra Gibbs free energy for a density fluctuation $\rho(x)$ is

$$\Delta G = \int \rho(x) (\mu[\rho(x)] - \mu_0) \, d^3x \tag{4}$$

since $\rho(x) \, d^3x$ is the number of particles that suffer the chemical potential rise $\mu[\rho(x)]$ in the volume $d^3x$. 

Fig. 2 Chemical potential: van der Waals. Chemical potential $\mu[\rho]$ of water fit with the van der Waals equation, at the boiling temperature of water $T = 373$ K and the corresponding van der Waals coexistence pressure $P = 1.5 \times 10^7$ dynes/cm$^2$.

(c) At room temperature, the interface between water and water vapor is very sharp: perhaps a molecule thick. This makes the whole idea of using a coarse-grained free energy problematical. Nonetheless, assuming an interfacial width of two or three Ångstroms, use the vdW model for the chemical potential (Fig. 2) and eqn 4 to roughly estimate the surface tension of water (the extra Gibbs free energy per unit area, roughly the barrier height times thickness). How does your answer compare with the measured value at the boiling point, 59 dynes/cm$^2$? (One mole = $6.023 \times 10^{23}$ molecules.)

Day 3

11.6 Coarsening in the Ising model. (Computation)

Coarsening is the process by which phases separate from one another; the surface tension drives tiny fingers and droplets to shrink, leading to a characteristic length scale that grows with time.

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3A link to the software can be found at the book Web site [2].
Start up the Ising model. Run with a fairly large system, demagnetize the system to a random initial state \((T = \infty)\), and set \(T = 1.5\) (below \(T_c\)) and run one sweep at a time. (As the pattern coarsens, you may wish to reduce the graphics refresh rate.) The pattern looks statistically the same at different times, except for a typical *coarsening length* that is growing. How can we define and measure the typical length scale \(L(t)\) of this pattern?

(a) Argue that at zero temperature the total energy above the ground-state energy is proportional to the perimeter separating up-spin and down-spin regions.\(^4\) Argue that the inverse of the perimeter per unit area is a reasonable definition for the length scale of the pattern.

(b) With a random initial state, set temperature and external field to zero. Measure the mean energy \(E(t)\) per spin as a function of time. Plot your estimate for \(L(t)\) in part (a) versus \(t\) on a log-log plot. (You might try plotting a few such curves, to estimate errors.) What power law does it grow with? What power law did we expect?

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References


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\(^4\)At finite temperatures, there is a contribution from thermally flipped spins, which should not really count as perimeter for coarsening.