

1. Please fill out the survey
2. i First, recall that

$$S = k_B \ln \Omega$$

$$dS = \frac{1}{T}dE + \frac{p}{T}dV - \frac{\mu}{T}dN$$

Now, let us consider an isolated system at an energy E and volume V . We focus on a small subsystem in this isolated system, that is much smaller than the rest of the system, which we call the bath. The subsystem is free to exchange energy and volume with the bath. The probability of finding the subsystem in a given microstate ν characterized by an energy E_ν volume V_ν is proportional to the number of bath states given this constraint

$$P(\nu) \propto \Omega_{\text{bath}}(E - E_\nu, V - V_\nu)$$

$$P(\nu) \propto \exp[\ln \Omega_{\text{bath}}(E - E_\nu, V - V_\nu)]$$

Now we just have to Taylor expand $\ln \Omega_{\text{bath}}$ about E and V . Also, let's define $\beta \equiv 1/k_B T$. We get

$$P(\nu) \propto \exp \left[\ln \Omega_{\text{bath}}(E, V) - \frac{\partial \ln \Omega_{\text{bath}}(E, V)}{\partial E} E_\nu - \frac{\partial \ln \Omega_{\text{bath}}(E, V)}{\partial V} V_\nu \right]$$

$$P(\nu) \propto \exp \left[-\frac{\partial \ln \Omega_{\text{bath}}(E, V)}{\partial E} E_\nu - \frac{\partial \ln \Omega_{\text{bath}}(E, V)}{\partial V} V_\nu \right]$$

$$P(\nu) \propto \exp \left[-\frac{1}{k_B} \frac{\partial S}{\partial E} E_\nu - \frac{1}{k_B} \frac{\partial S}{\partial V} V_\nu \right]$$

$$P(\nu) \propto \exp [-\beta E_\nu - \beta p V_\nu]$$

Therefore the partition function is just the sum over states ν .

$$\zeta = \sum_{\nu} e^{-\beta(E_\nu + pV_\nu)}$$

The probability of being in a state ν is simply

$$P(\nu) = \frac{e^{-\beta(E_\nu + pV_\nu)}}{\zeta}$$

- ii Another way of writing ζ is

$$\zeta = \sum_V e^{-\beta pV} Q(N, V, T)$$

where Q is the Canonical Ensemble partition function

$$Q(N, V, T) = \sum_{\nu} e^{-\beta E_\nu}$$

- iii Since in the thermodynamic limit, one V , V^* dominates ζ , we can approximate ζ as

$$\zeta = e^{-\beta pV^*} Q(V^*)$$

$$\zeta = e^{-\beta(pV^* + A(N, V^*, T))}$$

$$\zeta = e^{-\beta G}$$

$$\ln \zeta = -\beta G$$

where G is the Gibbs' Free Energy.

iv The derivative is

$$\begin{aligned}\left(\frac{\partial \ln \zeta}{\partial(\beta p)}\right)_{\beta, N} &= \left(-\sum_V V e^{-\beta p V} Q(N, V, T)\right) / \left(\sum_V e^{-\beta p V} Q(N, V, T)\right) \\ &= -\langle V \rangle\end{aligned}$$

We should get the same answer taking the derivative of our answer in part (iii).

$$\begin{aligned}\left(\frac{\partial \ln \zeta}{\partial(\beta p)}\right)_{\beta, N} &= \left(\frac{\partial -\beta G}{\partial \beta p}\right)_{\beta, N} \\ &= -\left(\frac{\partial G}{\partial p}\right)_{\beta, N}\end{aligned}$$

Since

$$dG = -SdT + Vdp + \mu dN$$

we have

$$\left(\frac{\partial \ln \zeta}{\partial(\beta p)}\right)_{\beta, N} = -V$$

v

$$\begin{aligned}\left(\frac{\partial^2 \ln \zeta}{\partial(\beta p)^2}\right)_{\beta, N} &= \left(\frac{\partial \left(-\sum_V V e^{-\beta p V} Q(N, V, T)\right) / \left(\sum_V e^{-\beta p V} Q(N, V, T)\right)}{\partial(\beta p)}\right)_{\beta, N} \\ &= \left(\sum_V V^2 e^{-\beta p V} Q(N, V, T)\right) / \left(\sum_V e^{-\beta p V} Q(N, V, T)\right) - \\ &\quad \left[\left(\sum_V V e^{-\beta p V} Q(N, V, T)\right) / \left(\sum_V e^{-\beta p V} Q(N, V, T)\right)\right]^2 \\ &= \langle V^2 \rangle - \langle V \rangle^2 \\ &= \langle \delta V^2 \rangle\end{aligned}$$

Additionally, we know that

$$\left(\frac{\partial \ln \zeta}{\partial(\beta p)}\right)_{\beta, N} = -V$$

Therefore

$$\begin{aligned}\left(\frac{\partial^2 \ln \zeta}{\partial(\beta p)^2}\right)_{\beta, N} &= -\left(\frac{\partial V}{\partial(\beta p)}\right)_{\beta, N} \\ &= -\frac{1}{\beta} \left(\frac{\partial V}{\partial p}\right)_{T, N} \\ &= k_B T V \kappa_T \\ \langle \delta V^2 \rangle &= k_B T V \kappa_T\end{aligned}$$

3. i In this problem, we are working in the isothermal-isobaric ensemble that we examined in Problem 2. Each microstate is defined by $\nu = \{l_1, l_2, \dots, l_{N-1}\}$. The probability of being in a microstate ν is

$$P_\nu \propto e^{-\beta(E_\nu + pL_\nu)}$$

Since the energies of each microstate are the same, we get

$$P_\nu = e^{-\beta p L_\nu}$$

$$\zeta = \sum_\nu e^{-\beta p L_\nu}$$

Since each of these spacings are uncorrelated, we can break up the sum into the sum over each l_i .

$$\zeta = \sum_{l_1} e^{-\beta p l_1} \sum_{l_2} e^{-\beta p l_2} \sum_{l_3} e^{-\beta p l_3} \dots \sum_{l_{N-1}} e^{-\beta p l_{N-1}}$$

Now the range of each l_i is

$$l_i = \{\sigma, \sigma + \Delta, \sigma + 2\Delta, \sigma + 3\Delta, \dots\}$$

Inputting this into the summations we get

$$\zeta = \left(\sum_{l=\sigma}^{\infty} e^{-\beta p l} \right)^{N-1}$$

Since we can assume $\Delta \ll \beta$, so we can approximate the sums as integrals

$$\zeta = \left(\frac{1}{\Delta} \int_{l=\sigma}^{\infty} e^{-\beta p l} \right)^{N-1}$$

$$\zeta = \left(\frac{1}{\Delta} \frac{1}{\beta p} e^{-\beta p \sigma} \right)^{N-1}$$

- ii T is a conjugate variable to E . Since all states are energetically the same, this would suggest that the partition function would not depend on T .
- iii First we know that

$$\left(\frac{\partial \ln \zeta}{\partial -\beta p} \right) = \langle L \rangle$$

Substituting in ζ computed in part [i], we get

$$\langle L \rangle = (N-1) \left[\frac{1}{\beta p} + \sigma \right]$$

Since $\rho = N/\langle L \rangle$,

$$\rho = \frac{N}{N-1} \left(\frac{1}{\beta p} + \sigma \right)^{-1}$$

In the limit that $N \gg 1$, we can simplify this to

$$\rho = \left(\frac{1}{\beta p} + \sigma \right)^{-1}$$

iv

$$\begin{aligned}
\langle(\delta L)^2\rangle &= \frac{\partial^2 \ln \zeta}{\partial \beta p^2} \\
&= \frac{\partial(N-1) \left[\frac{1}{\beta p} + \sigma \right]}{\partial - \beta p} \\
&= \frac{N-1}{(\beta p)^2} \\
&= \frac{N}{(\beta p)^2}
\end{aligned}$$

Now, rearranging ρ in terms of βp , we get

$$\frac{1}{\beta p} = \frac{1}{\rho} - \sigma$$

Then we get,

$$\langle(\delta L)^2\rangle = N \left(\frac{1}{\rho} - \sigma \right)^2$$

Now we can compare this to the fluctuations of the 1D ideal gas.

The equation of state for the ideal gas is

$$\begin{aligned}
pL &= k_B T N \\
L &= \frac{N}{\beta p}
\end{aligned}$$

Furthermore we know that $\rho = N/L = \beta p$. Therefore the fluctuations in the length for a 1D ideal gas are:

$$\begin{aligned}
\langle(\delta L_{\text{ideal}})^2\rangle &= -\frac{\partial L_{\text{ideal}}}{\partial \beta p} \\
&= N \left(\frac{1}{\beta p} \right)^2 \\
&= N \left(\frac{1}{\rho} \right)^2
\end{aligned}$$

which is the fluctuation in length for our rods as $\sigma \rightarrow 0$. Now as $\rho \rightarrow \sigma^{-1}$, we get that the fluctuations in length approach 0, as there can be no fluctuations when the rods are all in contact with each other.

v We determine the isothermal compressibility as

$$\kappa_T = -\frac{1}{L} \left(\left(\frac{\partial L}{\partial p} \right)_{T,N} \right)$$

Rearranging terms a little, we get,

$$\begin{aligned}\kappa_T &= -\frac{1}{L} \left(\left(\frac{\partial L}{\partial p} \right)_{T,N} \right) \\ &= -\frac{1}{L} \left(-\beta N \left(\frac{1}{\rho} - \sigma \right)^2 \right) \\ &= \beta \rho \left(\frac{1}{\rho} - \sigma \right)^2\end{aligned}$$

4. i Just like in Problem 2, the lengths are uncorrelated. We can therefore write the partition function as

$$\begin{aligned}\zeta &= \sum_{l_1} e^{-\beta(E_{l_1} + pl_1)} \sum_{l_2} e^{-\beta(E_{l_2} + pl_2)} \sum_{l_3} e^{-\beta(E_{l_3} + pl_3)} \dots \sum_{l_{N-1}} e^{-\beta(E_{l_{N-1}} + pl_{N-1})} \\ &= \left(\sum_l e^{-\beta(E_l + pl)} \right)^{N-1} \\ &= \left(e^{\beta\epsilon - \beta p\sigma} + \sum_{\sigma+\Delta} e^{-\beta pl} \right)^{N-1} \\ &= \left(e^{\beta\epsilon - \beta p\sigma} + \frac{1}{\Delta} \int_{\sigma+\Delta}^{\infty} e^{-\beta pl} dl \right)^{N-1}\end{aligned}$$

Using the assumption $\sigma + \Delta \approx \sigma$, and performing the integration we get

$$\zeta = \left(e^{-\beta p\sigma} \left(e^{\beta\epsilon} + (\Delta\beta p)^{-1} \right) \right)^{N-1}$$

- ii Just like before

$$\begin{aligned}-\langle L \rangle &= \left(\frac{\partial \ln \zeta}{\partial \beta p} \right)_{\beta, N} \\ \langle L \rangle &= (N-1) \left[\sigma + \frac{1}{\Delta\beta^2 p^2 e^{\beta\epsilon} + \beta p} \right] \\ \rho &= \left[\sigma + \frac{1}{\Delta\beta^2 p^2 e^{\beta\epsilon} + \beta p} \right]^{-1}\end{aligned}$$

(as $N \approx N-1$ in the thermodynamic limit).

- iii We can define an equivalence between P_{contact} and $\langle E \rangle$.

$$\begin{aligned}(N-1)P_{\text{contact}} &= -\frac{1}{\epsilon} \langle E \rangle \\ &= \left(\frac{\partial \ln \zeta}{\partial \beta \epsilon} \right)_{\beta p, N} \\ &= (N-1) \left[\frac{e^{\beta\epsilon}}{e^{\beta\epsilon} + (\Delta\beta p)^{-1}} \right] \\ P_{\text{contact}} &= \left[\frac{e^{\beta\epsilon}}{e^{\beta\epsilon} + (\Delta\beta p)^{-1}} \right]\end{aligned}$$

iv Substituting in the dimensionless parameters:

$$\begin{aligned} p^* &= \beta p \sigma \\ \rho^* &= \rho \sigma \\ a &= (\Delta/\sigma) e^{\beta \epsilon} \end{aligned}$$

We get

$$\rho^* = \left[1 + ((p^*)^2 a + p^*)^{-1} \right]^{-1}$$

The graph for ρ^* is shown in Fig. 1.

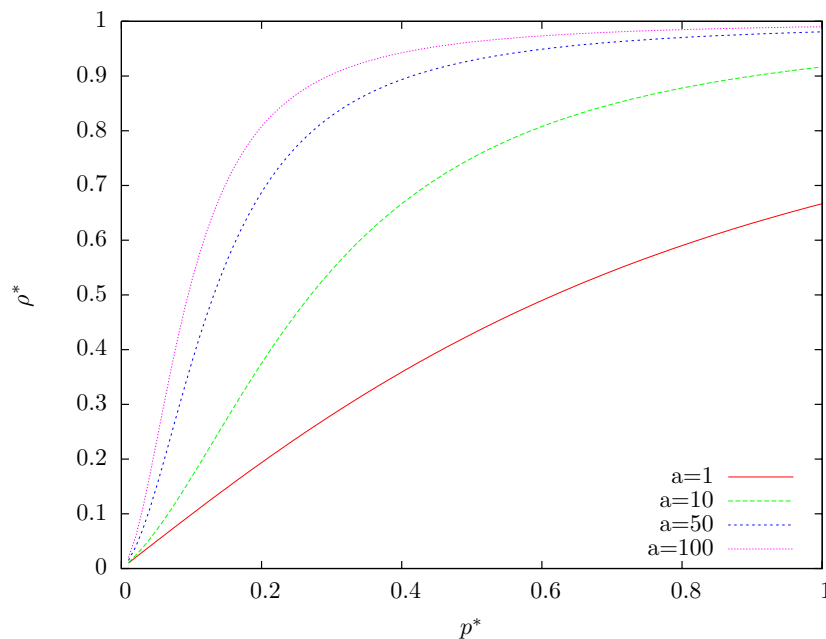


Figure 1: ρ^* as a function of p^*

Our dimensionless P_{contact} is,

$$P_{\text{contact}} = \frac{a}{a + \frac{1}{p^*}}$$

It is graphed in Fig. 2.

v From our first plot we see that the derivative: $\left(\frac{\partial \rho^*}{\partial p^*}\right)_{N,T} \geq 0$ $\left(\frac{\partial p^*}{\partial \rho^*}\right)_{N,T} \geq 0$ From definitions of ρ^*, p^*

$$\begin{aligned} \left(\frac{\partial \rho \sigma}{\partial \sigma p \beta}\right)_{N,T} &\geq 0 \\ \left(\frac{\partial \rho}{\partial p \beta}\right)_{N,T} &\geq 0 \end{aligned}$$

Since beta is just a constant and is always positive, we can pull it out and get rid of it because it doesn't change the sign.

$$\left(\frac{\partial \rho}{\partial p}\right)_{N,T} \geq 0$$

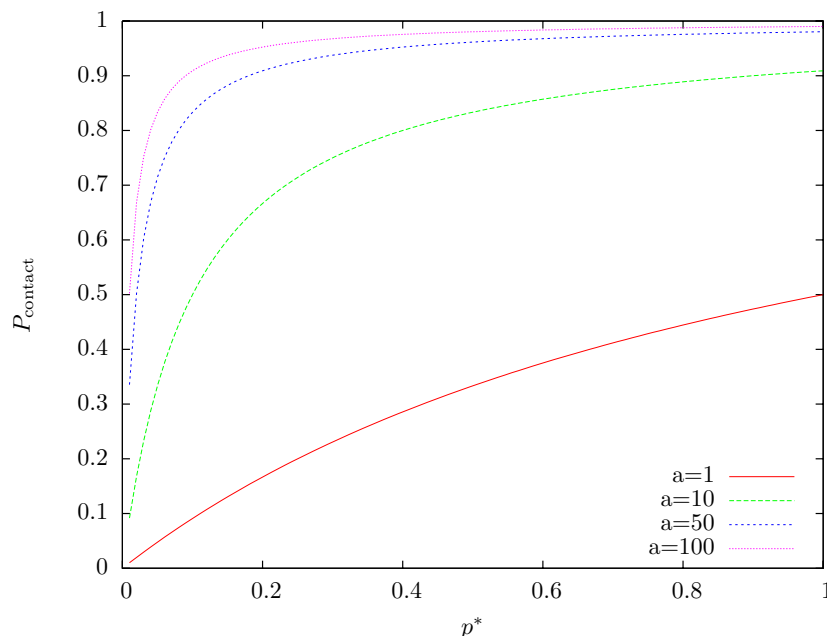


Figure 2: P_{contact} as a function of p^*

$$\rho = N/V$$

So,

$$\left(\frac{\partial N/V}{\partial p} \right)_{N,T} \geq 0$$

N , again, is a positive constant we can pull out and get rid of:

$$\left(\frac{\partial 1/V}{\partial p} \right)_{N,T} \geq 0$$

Chain rule:

$$-\frac{1}{V^2} \left(\frac{\partial V}{\partial p} \right)_{N,T} \geq 0$$

V^2 must be positive so let's throw that away as well.

$$-\left(\frac{\partial V}{\partial p} \right)_{N,T} \geq 0$$

Multiplying both sides by -1 (which SWITCHES the inequality to \leq) we see:

$$\left(\frac{\partial V}{\partial p} \right)_{N,T} \leq 0$$

Which is exactly what we want because we know this is true at equilibrium for V, P because of stability. So now we see that our 'equation of state' satisfies stability and therefore there is no "Volume" phase transition/discontinuity in this 1D model (nor in a 1D ideal gas). We'll come to learn later on that this is because defects/interfaces in the system do not grow with the system size (interfaces are usually $d-1$ dimensional so in

1D they are “0” dimensional) and thus can propagate freely. Thus, the system can avoid paying the high “cost” of an interface (– the surface tension) so easily that it is no longer a true barrier.

5. i The Metropolis scheme corresponds to the Canonical Ensemble. As we watch the Ising model over time in this scheme, we see that the system will eventually converge to the equilibrium state.

The Kawasaki scheme conserves the net magnetization of the sample. In the case where $J = 0$ this would be analogous to the Microcanonical Ensemble; however the energy does change due to changes in the interfacial energy.

- ii In order to get to a fixed density of $\rho = 0.2$ for the black phase, and a fixed density of $\rho = 0.8$ for the red phase, there are three required steps:
 1. Start in the *Metropolis* scheme at a $T > T_c$. For example $T = 3$ works. You should note that there is an equal density of both phases at this temperature
 2. Slowly cool down the sample, by reducing T . As you do this, you should one phase beginning to dominate over the other at approx $T = 2.3$ or so. This makes sense because as we cool the system below the critical temperature, we expect phase separation. Furthermore, since we have a finite system, we can begin to flip spins, engulfing smaller domains of one phase into larger domains of the other phase.
 3. Once you reach the point at which the ratio of densities is the target, switch over into the *Kawasaki* scheme, conserving the net magnetization (i.e. the density of each phase).
- iii At high temperatures, there are no persistent regions of one phase or the other-the entire system remains well mixed. This is because the thermal energy is greater than the coupling constant J (entropy wins out over enthalpy). At a temperature such as $T = 1.8$, we do observe persistent distinct phases.
- iv After a few minutes, we see a small decrease in the overall energy of the system. As we are in the *Kawasaki* scheme, the net magnetization does not change. However, the net length of phase interfaces is decreased, resulting in a lower energy.
- v One would expect consolidation of smaller regions of the minority phase, and a resultant decrease in the length of the interface and a reduction of said interfacial energy. The shapes of these domains we expect to become more condensed and to have smoother edges over time.
- vi After an hour at $T = 1.8$, we are quite close to equilibrium. We know from previous analyses that the equilibrium state of this system should have a domain wall that separates the two phases. We would expect this wall to be flat and for there to be minor fluctuations around this state.
- vii At high temperatures, we see minimal equilibration as the fluctuations are quite large, resulting in no domain wall formation. At lower temperatures there is moderate equilibration and at low temperatures, the system can reach this equilibrium state.