Lennard-Jones fluid

The aim of this practical is to calculate the Hemlholtz free energy $A = U - TS$ as a function of temperature for the Lennard-Jones fluid at $\rho = 0.8$. We will do this via thermodynamic integration (TI), modifying the LAMMPS example from this morning's lecture.

A reference state

The free energy of a fluid cannot be calculated directly from a molecular dynamics simulation. A TI calculation involves simulating a system under conditions where its absolute free energy can be calculated analytically to a very good approximation. These conditions are known as the *reference state*.

From here, we sample *derivatives* of the free energy along a path through the phase diagram which takes us to the temperature and density of interest. By integrating these derivatives along the path, we can compute the change in free energy relative to the reference state, and hence the absolute free energy of any point along the path.

Task 1: By modifying the LAMMPS example from the lecture this morning, identify a range of densities at a temperature of $T = 2.0$ over which the Lennard-Jones fluid is sufficiently dilute that the system behaves as an ideal gas. You should run LAMMPS calculations at a range of densities (hint - use a range which is uniform on a logarithmic scale) and plot the average pressure (with error bars) compared to that predicted by the ideal gas equation.

You might want to submit several jobs to the spacebat queue in parallel to speed up your workflow. You should only need a single processor core for each simulation. You should not need to run for more than a few hundred thousand timesteps, but may wish to use larger systems (e.g. 864 atoms) for improved statistics. Remember that we work in reduced units such that $k_B = 1$, and $\beta = 1/T$.

Theory: The partition function of the ideal gas is

$$Q_{\text{id}} = \frac{V^N}{N!h^{3N}} \left(\frac{2\pi m}{\beta}\right)^{3N/2} \tag{1}$$

or written in terms of the DeBroglie wavelength

$$Q_{\text{id}} = \frac{V^N}{N!\Lambda^{3N}} \tag{2}$$

which defines

$$\Lambda = h \left(\frac{\beta}{2\pi m}\right)^{1/2} \tag{3}$$

and the Helmholtz free energy becomes

$$\beta A_{\text{id}} = -\ln Q_{\text{id}} = 3N \ln \Lambda + \ln N! - N \ln V. \tag{4}$$

The contribution from the $3N \ln \Lambda$ term is constant at constant T and is usually set to zero (i.e. $\Lambda = 1$) by convention[1]. The free energy of the ideal gas reference state (per particle) for integrating along an isotherm is therefore taken as

$$\beta A_{\text{id}}/N = \ln \rho - 1. \tag{5}$$

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[1] This is because we are usually only interested in free energy *differences* between states. This term will always cancel when subtracting two free energies computed at the same temperature, so we don't bother carrying it around.

Integration along the $T = 2.0$ isotherm

Theory: The free energy at $\rho = 0.8$, where the system does not behave as an ideal gas, can be found by thermodynamic integration using samples of the pressure at a series of volumes, since

$$\left.\frac{\partial A}{\partial V}\right|_{N,V,T} = -P\left(N, V, T\right) \tag{6}$$

and so the change in Helmholtz free energy upon compression from V_1 (in this case the ideal gas reference state) to V_2 (at the density of interest) is

$$\Delta A = \int_{V_1}^{V_2} -P \, \mathrm{d}V \tag{7}$$

To integrate from the ideal gas to the fluid density of interest ($\rho = 0.8$) it is convenient to change integration variable to $x = \ln V$ giving

$$\Delta A = \int_{\ln V_1}^{\ln V_2} -P\mathrm{e}^{x} \, \mathrm{d}x = \int_{\ln V_1}^{\ln V_2} -PV \, \mathrm{d}x \tag{8}$$

Task 2: Choose a volume V_1 and hence density ρ_1 where your simulations behave as an ideal gas.

Using the series of simulations already conducted above, construct a plot of $-PV$ as a function of $\ln V$ between V_1 and V_2, where V_2 corresponds to a density of $\rho = 0.8$. You might find a spreadsheet helpful here if you are not an awk ninja.

Integrate this function numerically to obtain ΔA as a function of density ρ. If you need help with integrating the function then seek help. There are various ways of doing this using software on the system (e.g. xmgrace) or by writing a simple Python script.

Record your calculated value of A at $\rho = 0.8$ to use as a reference (A_{ref}) for a second thermodynamic integration below.

At this point you can validate your calculation by comparing to previous data . First use your data to calculate the chemical potential as a function of density along the $T = 2.0$ isotherm.

$$\mu(\rho) = T\left(\ln \rho_1 - 1\right) + \Delta A(\rho)/N + P\left(\rho\right)/\rho \tag{9}$$

Subtract from this the chemical potential of an ideal gas under at the same temperature and density. Note that the ideal gas will be under a different pressure at this density, $P_{\mathrm{id}}\left(\rho\right)$

$$\mu_{\mathrm{id}}(\rho) = T\left(\ln \rho - 1\right) + P_{\mathrm{id}}\left(\rho\right)/\rho_{\mathrm{id}}. \tag{10}$$

The result $\mu_{ex} = \mu_{\mathrm{LJ}} - \mu_{\mathrm{id}}$ can be compared to an equation of state by Johnson *et al* as in figure 1.

Can you estimate the uncertainty in your calculations of μ_{ex} from the error bars on each individual calculation of average pressure?

Integration along the $\rho = 0.8$ isochore

Theory: Given a reference free energy at the desired density and at $T = 2.0$, we can compute $A(T)$ along the $\rho = 0.8$ isochore.

$$\left.\frac{\partial\left(\beta A\right)}{\partial \beta}\right|_{N,V,T} = E(N,V,T). \tag{11}$$

We will integrate to $T = 2.0$ from $T = 1.0$.

$$\Delta\left(\beta A\right) = \int_{\beta=1/2}^{\beta=1} E(N,V,T)\ \mathrm{d}\beta \tag{12}$$

transforming into an integral over temperature

$$\Delta\left(\beta A\right) = \int_{T=2}^{T=1} -\frac{E(N,V,T)}{T^2}\ \mathrm{d}T \tag{13}$$

If taking $\Lambda = 1$ as above, we can ignore the contribution from the kinetic energy and use

$$\Delta\left(\beta A\right) = \int_{T=2}^{T=1} -\frac{U(N,V,T)}{T^2}\ \mathrm{d}T. \tag{14}$$

Task 3: Construct a series of LAMMPS simulations at $\rho = 0.8$ for temperatures between $T = 2.0$ and $T = 1.0$ and compute the average potential energy U. As before, tabulate this and integrate (as in equation 14) to obtain the change in βA along the isochore.

Convert this to an absolute chemical potential (under the convention $\Lambda = 1$) rather than an excess. The pressure at each temperature is readily obtained from the simulations.

$$\beta\mu\left(T\right) = \left(\beta A\right)_{\text{ref}} + \Delta\left(\beta A\right)\left(T\right) + \beta P\left(T\right)/\rho \tag{15}$$

Example results are compared to the Johnson et al equation of state in figure 2. In these data the error bars on the computed chemical potential are smaller than the size of the points.

If your results do not agree with those shown to within error, then consider the possible sources of miscalculation.

- Have you excluded the equilibration portion of each simulation when, computing averages? The length of this portion will vary with ρ and T.
- Have you visualised your simulations to check for any obvious mistakes?
- Have you accounted for correlations in your data when computing the size of your error bar?
- Have you taken enough samples of the energy/pressure to minimise integration error?
- Do your simulations use too large a timestep, or an unsuitable choice of the thermostat coupling parameter?

Spoilers!

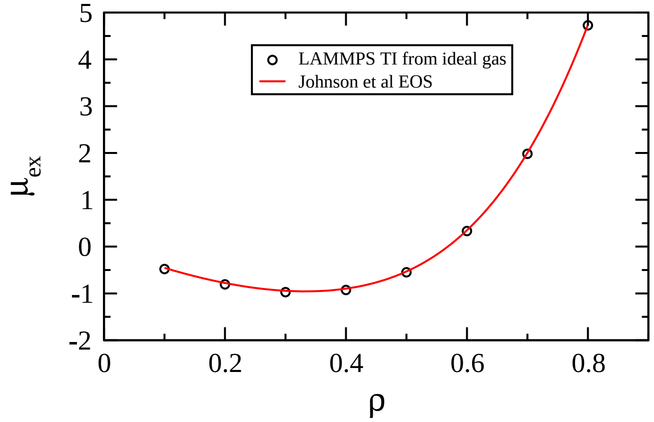

Figure 1: Excess chemical potential along the Lennard-Jones $T = 2.0$ isotherm via thermodynamic integration from the ideal gas limit. The equation of state by Johnson *et al* is shown for comparison.

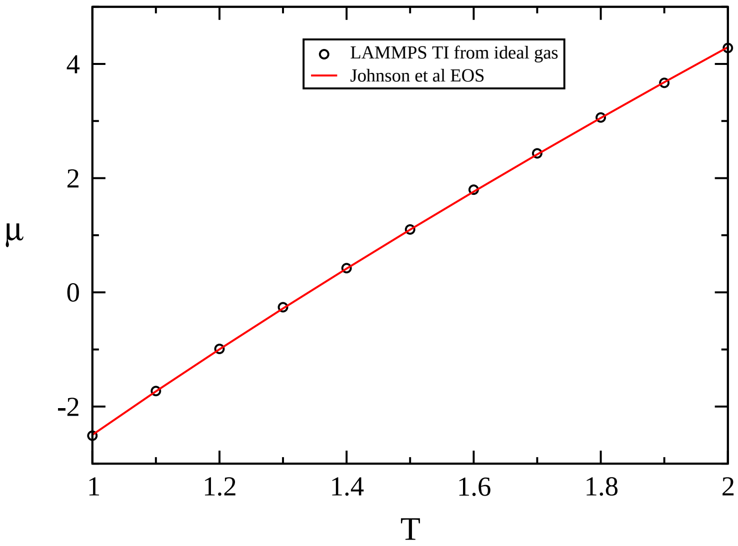

Figure 2: Chemical potential for the Lennard-Jones fluid along the $\rho = 0.8$ isochore, as computed by thermodynamic integration from the ideal gas, compared to the equation of state by Johnson *et al*.