

## CE 530

### Assignment #3 Solution

1. The isothermal-isobaric partition function is:

$$\Delta(T, p, N) = \frac{1}{\Lambda^3} \int_0^{\infty} dV \int_V d\mathbf{r}^N e^{-\beta pV} e^{-\beta U(\mathbf{r}^N)}$$

Using the bridge equation,  $G = -kT \ln \Delta$ , show that the thermodynamic relation

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

yields an expression representing the average of volume in this ensemble.

$$\begin{aligned} V &= \left( \frac{\partial G}{\partial p} \right)_{T, N} \\ &= -\frac{\partial}{\partial p} kT \ln \Delta \\ &= -\frac{kT}{\Delta} \frac{\partial}{\partial p} \Delta \\ &= -\frac{kT}{\Delta} \frac{\partial}{\partial p} \left[ \frac{1}{\Lambda^3} \int_0^{\infty} dV \int_V d\mathbf{r}^N e^{-\beta pV} e^{-\beta U(\mathbf{r}^N)} \right] \\ &= -\frac{kT}{\Delta} \left[ \frac{1}{\Lambda^3} \int_0^{\infty} dV \int_V d\mathbf{r}^N \left( \frac{\partial}{\partial p} e^{-\beta pV} \right) e^{-\beta U(\mathbf{r}^N)} \right] \\ &= -\frac{kT}{\Delta} \left[ \frac{1}{\Lambda^3} \int_0^{\infty} dV \int_V d\mathbf{r}^N \left( (-\beta V) e^{-\beta pV} \right) e^{-\beta U(\mathbf{r}^N)} \right] \\ &= -\frac{kT(-\beta)}{\Delta} \left[ \frac{1}{\Lambda^3} \int_0^{\infty} dV \int_V d\mathbf{r}^N \left( (V) e^{-\beta pV} \right) e^{-\beta U(\mathbf{r}^N)} \right] \\ &= \frac{1}{\Delta} \left[ \frac{1}{\Lambda^3} \int_0^{\infty} dV \int_V d\mathbf{r}^N V e^{-\beta pV} e^{-\beta U(\mathbf{r}^N)} \right] \\ &= \langle V \rangle \end{aligned}$$

2. For an ideal gas the intermolecular potential is zero for all configurations. As a consequence the partition function is greatly simplified, and can be evaluated analytically. Do this for the canonical (NVT), isothermal-isobaric (NPT), and grand-canonical ( $\mu$ -VT) ensembles, and for each derive the ideal-gas equation of state  $PV = nRT$ .

As a bonus problem you might wish to do the same for the microcanonical (EVN) ensemble (Hint: you'll need the formula for the surface area of a hypersphere in arbitrary dimension to fully evaluate the partition function, but you don't need this to get the equation of state).

The canonical ensemble partition function is

$$Q(T, V, N) = \frac{1}{\Lambda^{3N}} \frac{1}{N!} \int d\mathbf{r}^N e^{-\beta U(\mathbf{r}^N)}$$

For an ideal gas, the function  $U(\mathbf{r}^N)$  is identically zero, so the integrand is simply unity, and the integral corresponds to unweighted the movement of each particle over the entire system volume. For each particle the integral evaluates to  $V$ , and for the collection of particles the full configurational integral is simply  $V^N$ , so

$$Q(T, V, N) = \frac{V^N}{\Lambda^{3N} N!}$$

The pressure is given as the derivative of the Helmholtz free energy, and with the bridge equation we have

$$\begin{aligned} P &= - \left( \frac{\partial A}{\partial V} \right)_{T, N} \\ &= kT \left( \frac{\partial \ln Q}{\partial V} \right)_{T, N} \\ &= kT \left( \frac{\partial \ln(V^N / \Lambda^{3N} N!)}{\partial V} \right)_{T, N} \\ &= kT \left( \frac{\partial \ln(V^N)}{\partial V} \right)_{T, N} \\ &= \frac{NkT}{V} = \frac{nRT}{V} \end{aligned}$$

where  $n = N / N_{Avogadro}$  is the number of moles, and we recall that the gas constant and Boltzmann's constant are related through Avogadro's number:  $R = kN_{Avogadro}$

For the isothermal-isobaric ensemble, the partition function is

$$\Delta(T, P, N) = \int_0^{\infty} dV Q(T, V, N) e^{-PV/kT}$$

With the result above for the ideal-gas canonical partition function  $Q$ , this becomes

$$\Delta(T, P, N) = \int_0^{\infty} dV \frac{V^N}{\Lambda^{3N} N!} e^{-PV/kT}$$

The integral can be evaluated analytically, using the general formula  $\int_0^{\infty} x^n e^{-ax} dx = n! / a^{n+1}$

$$\Delta(T, P, N) = \frac{(kT)^{N+1}}{\Lambda^{3N} P^{N+1}}$$

We apply thermodynamics and the bridge equation to get the volume in terms of the pressure

$$\begin{aligned} V &= \left( \frac{\partial G}{\partial P} \right)_{T, N} \\ &= -kT \left( \frac{\partial \ln \Delta}{\partial P} \right)_{T, N} \\ &= +kT \left( \frac{\partial \ln [P^{N+1} / (kT)^{N+1} \Lambda^{3N}]}{\partial P} \right)_{T, N} \\ &= kT \left( \frac{\partial \ln P^{N+1}}{\partial P} \right)_{T, N} \\ &= \frac{(N+1)kT}{P} \end{aligned}$$

This result is *slightly* different from the canonical-ensemble result (and the “true” ideal gas law), in that we have  $N+1$  where we would normally have just  $N$ . This is an example of how statistical mechanics gives slightly inconsistent results when dealing with small system sizes. In the thermodynamic limit,  $N \rightarrow \infty$ , the difference is completely negligible.

For the grand-canonical ensemble, the partition function is

$$\Xi(T, V, \mu) = \sum_{N=0}^{\infty} Q(T, V, N) e^{\mu N/kT}$$

and with the ideal-gas canonical-ensemble partition function

$$\Xi(T, V, \mu) = \sum_{N=0}^{\infty} \frac{V^N}{\Lambda^{3N} N!} e^{\mu N/kT}$$

The sum can be performed analytically, using  $\sum_{n=0}^{\infty} x^n / n! = e^x$

$$\Xi(T, V, \mu) = \exp \left[ \frac{V}{\Lambda^3} e^{\mu/kT} \right]$$

The bridge equation gives the pressure directly

$$\begin{aligned} PV &= kT \ln \Xi \\ &= kT \left[ \frac{V}{\Lambda^3} e^{\mu/kT} \right] \\ P &= \frac{kT}{\Lambda^3} e^{\mu/kT} \end{aligned}$$

In the last equality the quantity on the right is known as the *fugacity*, and this formula shows that for an ideal gas it equals the pressure. To get the ideal-gas equation of state, we need to do a derivative to get the number of molecules, thus

$$\begin{aligned} N &= \left( \frac{\partial(PV)}{\partial\mu} \right)_{T,V} \\ &= kT \left( \frac{\partial \ln \Xi}{\partial\mu} \right)_{T,V} \\ &= kT \left( \frac{\partial \left[ \frac{V e^{\mu/kT}}{\Lambda^3} \right]}{\partial\mu} \right)_{T,V} \\ &= \frac{V}{\Lambda^3} e^{\mu/kT} \end{aligned}$$

Comparing this with the equation for the pressure, we can eliminate  $e^{\mu/kT} / \Lambda^3$ , and get the ideal gas law,  $P = NkT / V$ .

To get the ideal-gas partition function in the microcanonical ensemble, we have to return to its definition as the number of states of given energy  $E$  for  $N$  molecules in a volume  $V$ . We can write the partition function as

$$\Omega(E, V, N) = \int d\mathbf{p}^N \delta \left( E - \sum \mathbf{p}_i^2 / 2m \right) \int d\mathbf{r}^N$$

where  $\delta$  is the Dirac delta function, and has the effect of allowing contributions to the integral only when its integrand is zero. The atom positions  $\mathbf{r}^N$  don't affect the energy, so the configurational integral can be done as before, giving a term  $V^N$ . Let's rewrite the integral to take out the  $2m$  term

$$\Omega(E, V, N) = V^N (2m)^{3N/2} \int d\mathbf{x}^N \delta \left( E - \sum x_i^2 \right)$$

This indicates we sum over all  $x$  such that their square equals a constant. This constraint describes the surface of a sphere in  $3N$  dimensions, of radius  $E^{1/2}$ . So the integral is just the surface area of a  $3N$ -dimensional hypersphere:  $S_N = (2\pi)^{3N/2} E^{3N/2} / \Gamma(3N/2)$ , and

$$\Omega(E, V, N) = V^N (4\pi m)^{3N/2} E^{3N/2}$$

We need the  $E$ -dependence to get the temperature

$$\begin{aligned} 1/T &= \left( \frac{\partial S}{\partial E} \right)_{V, N} \\ &= k \left( \frac{\partial \ln \Omega}{\partial E} \right)_{V, N} \\ &= k \left( \frac{\partial \ln [V^N (4\pi m)^{3N/2} E^{3N/2}]}{\partial E} \right)_{V, N} \\ &= k \left( \frac{\partial \ln E^{3N/2}}{\partial E} \right)_{V, N} \\ &= \frac{3}{2} Nk / E \end{aligned}$$

This gives the usual equipartition results  $E = \frac{3}{2} NkT$ . Likewise, the pressure is given by

$$\begin{aligned} \frac{P}{T} &= \left( \frac{\partial S}{\partial V} \right)_{E, N} \\ &= \frac{Nk}{V} \end{aligned}$$

Which gives the ideal-gas law without all the hypersphere stuff!