QUALIFYING EXAMINATION, Part 3

Solutions

Problem 1: Statistical Mechanics I

(a) $S = k_B N \log 6$

(b) $Z = e^{N\epsilon/k_BT} + 6^N$

(c) In general, $P_f = e^{N\epsilon/k_BT}/Z$.
After some algebra we find:
$T_{0.5} = \frac{\epsilon}{k_B \log 6}$ and
$T_{0.1} = \frac{\epsilon}{k_B \log 6 - k_B/N \log 9}$

(d) By construction, in our model both the entropy of the unfolded state and the energy of the folded one are linear in N, so $T_{0.5}$ does not depend on N. However, because this model assumes that the entire polymer must fold together, the unfolding transition becomes sharper as N increases.

(e) In general, $P_u = 6^N/Z$, so that taking derivatives yields

$$g = T\frac{\partial P_u}{\partial T} = \frac{6^N e^{N\epsilon/k_BT}}{Z^2}\frac{N\epsilon}{k_BT} \ .$$

Substituting the solution for $T_{0.5}$ gives

$$g_{0.5} = \frac{N}{4}\log 6 \ .$$

(f) We have $T_{0.1} = \frac{\epsilon}{k_B \log 6 - k_B/N \log 9}$, $T_{0.9} = \frac{\epsilon}{k_B \log 6 + k_B/N \log 9}$ and $T_{0.1}/T_{0.9} = 1.01$. Dividing the first two equations, and substituting the third yields

$$1.01 = \frac{\log 6 + \log 9/N}{\log 6 - \log 9/N} \ ,$$

or

$$0.01 \log 6 = 2.1/N \log 9 \ .$$

We find $N \approx 250$. Physically, this model is not sufficiently accurate but we would expect a polymer of length in the hundreds to enact such a mechanism.

Problem 2: Statistical Mechanics II

(a) Using $PV = Nk_\mathrm{B}T$ and $E = \frac{3}{2}Nk_\mathrm{B}T$, we have $PV = \frac{2}{3}E$. Hence

$$H = E + PV = \frac{5}{2}PV = \frac{5}{2}Nk_\mathrm{B}T\ .$$

Since $T \propto H/N$, we find $\mu_\mathrm{JT} = \left(\frac{\partial T}{\partial P}\right)_H = 0$.

(b) The Bose-Einstein occupation $n(\epsilon)$ must be positive, hence $\epsilon - \mu > 0$ for all single-particle energy levels ϵ. This inequality is most stringent for the lowest energy level, i.e., the single-particle ground state in the box with energy ϵ_0. Since $\epsilon_0 \propto L^{-2}$ (where L is the box size), ϵ_0 tends to zero in the limit of a large box and $\mu \leq 0$.

At fixed β, $n(\epsilon)$ is largest when $\mu = 0$. In that case, the upper bound is

$$\begin{aligned} N_c &= \int_0^\infty \mathrm{d}\epsilon\ \mathcal{D}(\epsilon)n(\epsilon) = \frac{V}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\int_0^\infty \mathrm{d}\epsilon\ \frac{\sqrt{\epsilon}}{e^{\beta\epsilon}-1} \\ &= \frac{V}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\beta^{-3/2}\int_0^\infty \mathrm{d}x\ \frac{\sqrt{x}}{e^x-1} = \frac{V}{\lambda_T^3}\zeta\left(\frac{3}{2}\right)\ . \end{aligned}$$

Thus $\rho_c = N_c/V = \zeta(\frac{3}{2})/\lambda_T^3$.

(c) If atoms are added at fixed T beyond the critical density ρ_c, they accumulate in the single-particle ground state, forming a Bose-Einstein condensate.

(d) The thermal energy in the Bose-Condensed phase (for which $\mu = 0$) is

$$\begin{aligned} E &= \int_0^\infty \mathrm{d}\epsilon\ \epsilon\mathcal{D}(\epsilon)n(\epsilon) = \frac{V}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\int_0^\infty \mathrm{d}\epsilon\ \frac{\epsilon^{3/2}}{e^{\beta\epsilon}-1} \\ &= \frac{V}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\beta^{-5/2}\int_0^\infty \mathrm{d}x\ \frac{x^{3/2}}{e^x-1} \propto T^{5/2}\ . \end{aligned}$$

Also, in the Bose-condensed phase $N_\mathrm{ex} = N_c = \frac{V}{\lambda_T^3}\zeta\left(\frac{3}{2}\right) \propto T^{3/2}$. Since $E \propto T^{5/2}$, we have $E \propto N_\mathrm{ex}k_\mathrm{B}T$. The contribution to the energy is solely due to the particles in the excited states since the energy of the atoms in the Bose-Einstein condensate is zero in the limit of a large box.

(e) Since $h \propto E/N$ for the classical ideal gas, a process in which E/N is constant is isoenthalpic.

Comment: Using the grand potential, one can show that $PV = \frac{2}{3}E$ also holds for the ideal Bose gas, so the same conclusion holds for the ideal Bose gas.

(f) We saw in (d) that $E \propto N_{\text{ex}}T$. In the Bose-condensed phase $N_{\text{ex}} = N_c$ so that a process which keeps E/N constant also keeps N_cT/N constant. However, we saw in (b) that $N_c \propto T^{3/2}$. Thus the loss process keeps $T^{5/2}/N$ constant, so that $\gamma = -5/2$. The quantum Joule-Thomson process for an ideal Bose gas is thus a cooling process. Quantum correlations are sufficient to create a non-trivial JT effect, and interactions are not necessary unlike in the classical case.

Unfortunately the phase space density $\rho\lambda_T^3 \propto N/T^{3/2} \propto T(N/T^{5/2})$ decreases too.