MASSACHUSETTS INSTITUTE OF TECHNOLOGY

Physics Department

8.044 Statistical Physics I — Spring Term 2013

Solutions to Problem Set #7

Problem 1: Free Expansion of a Gas

a) No work is done, so $\Delta W = 0$. No heat enters the gas so $\Delta Q = 0$.
Thus $\Delta E = \Delta W + \Delta Q = 0$. <u>The internal energy is conserved.</u>

b) $E(T, V)$ is a state function; compare it before and after expansion in equilibrium situations.

$$
\begin{aligned}
dE &= TdS - PdV = \underbrace{T\left(\frac{\partial S}{\partial T}\right)_V}_{C_V} dT + \left(T\left(\frac{\partial S}{\partial V}\right)_T - P\right) dV \\
C_V &= \frac{3}{2}Nk \\
\left(\frac{\partial S}{\partial V}\right)_T &= \left(\frac{\partial P}{\partial T}\right)_V = \frac{Nk}{V - bN} \qquad \text{using a Maxwell relation} \\
dE &= \frac{3}{2}Nk\,dT + a\left(\frac{N}{V}\right)^2 dV \\
E &= \frac{3}{2}NkT - \frac{aN^2}{V} + constant
\end{aligned}
$$

When equating E before and after the constant cancels out.

$$
\begin{aligned}
\frac{3}{2}NkT_i - \frac{aN^2}{(V_0/3)} &= \frac{3}{2}NkT_f - \frac{aN^2}{V_0} \\
\frac{3}{2}Nk(T_f - T_i) &= -\frac{2aN^2}{V_0} \\
T_f &= \underline{T_i - \frac{4}{3}\frac{a}{k}\left(\frac{N}{V_0}\right)}
\end{aligned}
$$

The gas cools!

Problem 2: Use of a Carnot Cycle

a) Carnot Cycle $\Rightarrow dS_H = -dS_C \Rightarrow đQ_H/T_H = -đQ_C/T_C$. Use $dQ = C_0\,dT$.

$$\begin{aligned}
\Delta S_{body\ 1} &= -\Delta S_{body\ 2} \\
\int_{T_H}^{T_F} \frac{C_0}{T}\,dT &= -\int_{T_C}^{T_F} \frac{C_0}{T}\,dT \\
\ln\frac{T_F}{T_H} &= -\ln\frac{T_F}{T_C} \quad = \quad \ln\frac{T_C}{T_F} \\
\frac{T_F}{T_H} &= \frac{T_C}{T_F} \\
T_F &= \underline{\sqrt{T_H T_C}}
\end{aligned}$$

b)

$$\begin{aligned}
\Delta W_{out} &= |\Delta Q_H| - |\Delta Q_C| \\
W_{out} &= \int_{T_F}^{T_H} C_0\,dT - \int_{T_C}^{T_F} C_0\,dT \quad = \quad C_0\left[(T_H - T_F) - (T_F - T_C)\right] \\
&= C_0\,(T_H - 2T_F + T_C) \quad = \quad C_0\,(T_H - 2\sqrt{T_H T_C} + T_C) \\
&= \underline{C_0\,(\sqrt{T_H} - \sqrt{T_C})^2 \quad > \ 0}
\end{aligned}$$

Problem 3: Cooling Liquid Helium

a) Since the system is thermally isolated and no work is done in the process, the heat gained by the salt must equal the heat lost by the liquid.

$$
\begin{aligned}
\Delta Q_S &= -\Delta Q_L \\
\int_{T_0}^{1/2} bT^{-2}\,dT &= -\int_1^{1/2} aT^3\,dT \\
-b\Big[_{T_0}^{1/2} T^{-1} &= -\frac{a}{4}\Big[_1^{1/2} T^4 \\
\left(2-\frac{1}{T_0}\right) &= \frac{1}{4}\frac{a}{b}\left(\frac{1}{16}-1\right) = \frac{1}{4}\frac{a}{b}\frac{15}{16} = \frac{1}{4}\frac{128}{15}\frac{15}{16} = -2 \\
1/T_0 &= 4 \;\rightarrow\; \underline{T_0 = 1/4}
\end{aligned}
$$

b) Entropy is a state function, so one may compute its change by assuming the process was quasi-static. We will use $dS = đQ/T = C\,dT/T$.

$$
\begin{aligned}
\Delta S &= \Delta S_S + \Delta S_L \\
&= \int_{T_0}^{1/2} bT^{-3}\,dT + \int_1^{1/2} aT^2\,dT \\
&= -\frac{b}{2}\Big[_{1/4}^{1/2} T^{-2} + \frac{a}{3}\Big[_1^{1/2} T^3 \\
&= -\frac{b}{2}\underbrace{(4-16)}_{-12} + \frac{a}{3}\underbrace{\left(\frac{1}{8}-1\right)}_{-7/8} = \underline{6b-(7/24)a}
\end{aligned}
$$

Problem 4: Torsional Pendulum

a) First find the Hamiltonian.

$$\mathcal{H} = T + V + \frac{1}{2} I\dot{\theta}^2 + \frac{1}{2} K(\theta - \theta_0)^2$$

Then use the canonical ensemble expression for the probability density.

$$\begin{aligned} p(\theta, \dot{\theta}) &\propto \exp[-\frac{\mathcal{H}}{kT}] \\ &\propto \exp[-\frac{\dot{\theta}^2}{2(kT/I)}] \exp[-\frac{(\theta - \theta_0)^2}{2(kT/K)}] \end{aligned}$$

Notice two important features of this result. First, the probability density factors, $p(\theta, \dot{\theta}) = p(\theta)p(\dot{\theta})$, so θ and $\dot{\theta}$ are statistically independent. Second, the dependence on both θ and $\dot{\theta}$ has the Gaussian form. In particular, $p(\theta)$ is Gaussian with mean θ_0 and variance $\sigma_\theta^2 = kT/K$. Therefore,

$$\underline{< (\theta - \theta_0)^2 >^{1/2} = \sqrt{\frac{kT}{K}}}.$$

b) Since θ and $\dot{\theta}$ are statistically independent, $< \theta\dot{\theta} > = < \theta > < \dot{\theta} >$. By inspection, $p(\dot{\theta})$ is a zero-mean Gaussian, so $< \dot{\theta} > = 0$ which leads to $\underline{< \theta\dot{\theta} > = 0}$.

Problem 5: The Hydrogen Atom

a)

$$\mathcal{H}|n,l,m>= -\frac{A}{n^2}|n,l,m>$$

The lowest energy, $-A$, corresponds to $|1,0,0>$ and is non-degenerate. The next lowest energy, $-A/4$, is four fold degenerate:

$$|2,0,0>, \quad |2,1,1>, \quad |2,1,0>, \quad \text{and } |2,1,-1>.$$

The ratio of the number of atoms in the first excited energy level to the number in the ground state depends on both the energies and the degeneracies.

$$\frac{N(-A/4)}{N(-A)} = \frac{4\exp[A/4kT]}{\exp[A/kT]} = 4\exp[-(3/4)A/kT]$$

Using the conversion factor 1meV = 11.6K we find that 13.6eV = 1.58×10^5K. Evaluating the above ratio gives 4.8×10^{-170} at 300K and 1.6×10^{-51} at 1000K.

b) The degeneracy of the n^{th} energy level is

$$1 + 3 + 5 + \cdots + (2n-1) = n^2.$$

The partition function for a single atom, neglecting the unbound states, is

$$Z = \sum_{\text{states } i} \exp[-\epsilon_i/kT] = \sum_{n=1}^{\infty} n^2 \exp[\alpha/n^2],$$

where $\alpha \equiv A/kT$. Since $\alpha > 0$, it follows that $\exp[\alpha/n^2] > 1$ for all n. Using this we can set a lower bound for Z, but Z diverges since the lower bound diverges.

$$\underline{Z > \sum_{n=1}^{\infty} n^2 \qquad \text{which diverges}}$$

c) The Coulomb potential is a mathematical oddity in that it produces an infinite number of bound states with energies less than zero. This situation if modified in the real world by the presence of walls (consider the energy levels of a particle in a box) or by the presence of other atoms. The existence of hydrogen atoms in the interstellar medium, on the other hand, probably has more to do with the absence of excitation mechanisms (non-equilibrium) than with the presence of neighboring atoms.

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