PHYS 449 - Statistical Mechanics I
Midterm Solutions

Part 2: Each question is worth 30 points (30 points total)

1. (a) Initially we have an ideal gas satisfying the equation of state $PV = nk_BT$ and mean energy $U = (f/2)nk_BT$, where $f$ counts the number of degrees of freedom. Suddenly it expands into a volume $3V$. There is no heat associated with this ($Q = 0$), because the total box is thermally isolated. Is there work done? One might naively expect the work to be $-P\Delta V = -P(3V - V) = -2PV$. But the initial and final pressures are not equal! The initial pressure is $P_i = nk_BT/V$, and the final pressure is $P_f = nk_BT/3V = P_i/3$. Wait: what about the temperature? The act of removing the partition cannot change the mean kinetic energy of the particles, because they are just bouncing around and don’t care about the volume they occupy ($U$ is independent of $V$ in the equipartition theorem). So this means that the temperature is the same before and after, and that $\Delta U = 0$. So the work is $W = -(P_fV_f - P_iV_i) = -[(P/3)(3V) - PV]$; alternatively, $\Delta U = 0 = Q + W = W = 0$.

The change in entropy can be obtained using the really simple estimate $\Omega = (V/\Delta V)^N$, where $\Delta V$ is the size of a little volume region (roughly to quantize space). Then

$$\Delta S = Nk_B \left[ \ln \left( \frac{V_f}{\Delta V} \right) - \ln \left( \frac{V_i}{\Delta V} \right) \right] = Nk_B \ln \left( \frac{V_f}{V_i} \right) = Nk_B \ln \left( \frac{3V}{V} \right) = Nk_B \ln(3).$$

In other words, there are now two equivalent places (on either side of the original partition) for a particle to be, whereas at first there was only one. A more fancy way to obtain this result is to use the more complicated form for the entropy that came from the energy eigenvalues for a particle in a 3D box:

$$S = Nk_B \ln \left( \frac{4\pi}{3} \left( \frac{mU}{\hbar^2} \right)^{3/2} \right) = Nk_B \ln(junk) + Nk_B \ln(V), \quad (1)$$

keeping only the $V$-dependence of the entropy. The rest is obvious.

(b) Now the piston is pulled out slowly. It can’t be done isothermally, because this would require that the decreased energy associated with the work done by the gas would be compensated by heat entering the system, and this is impossible because the system is thermally isolated. So we know the system must cool down. Because there is no heat flow, the expansion must be adiabatic, independent of the speed at which the piston moves. So we can use the handy relations in the notes, $V_fT_f^{f/2} = V_iT_i^{i/2}$ and $P_fV_f^\gamma = P_iV_i^\gamma$ where $\gamma = (f+2)/f$. The first gives $3VT_f^{f/2} = VT_i^{i/2}$ or a final temperature $T_f = T/3^{f/2} < T$ as expected (energy goes down). The final pressure is found using $P_f(3V)^\gamma = P_iV_i^\gamma$ or $P_f = P/3^\gamma < P$, also as expected. The mean energy per particle after the expansion is $U = (f/2)nk_BT/3^{2/2}$. Because the heat is zero ($Q = 0$), the work done by the gas is

$$W = \Delta U - Q = \Delta U = \frac{f}{2} Nk_BT \left( \frac{1}{3^{2/2}} - 1 \right),$$

which is negative as expected. Alternatively, we could calculate the work the long way:

$$W = -\int_{V_i}^{V_f} PdV = -c \int_{V_i}^{V_f} \frac{dV}{V^\gamma} = -\frac{c}{\gamma - 1} \left( V_f^{-\gamma+1} - V_i^{-\gamma+1} \right) = \frac{c}{\gamma - 1} \left( (3V)^{-\gamma+1} - V^{-\gamma+1} \right)$$

Now, we know that $PV^\gamma = c$ so that $V^{-\gamma} = P/c$ or $V^{-\gamma+1} = PV/c$. Substituting this into the equation above gives

$$W = \frac{cPV}{c(\gamma - 1)} (3^{1-\gamma} - 1).$$
Because $\gamma = (f + 2)/f$ we have $1 - \gamma = (f - f - 2)/f = -2/f$ so that

$$W = \frac{f}{2} P V \left( \frac{1}{3^2/T} - 1 \right) = \frac{f}{2} N k_B T f \left( \frac{1}{3^2/T} - 1 \right),$$

which is consistent with the quick way above, based on energy considerations.

Last is the entropy. The easy answer is that for adiabatic processes, the change in entropy is given by the Clausius relation $\Delta S = Q/T$; if $Q = 0$ then $\Delta S = 0$ as well. Indeed, many people consider adiabatic processes to be equivalent to isentropic processes. That said, the temperature is not a constant here, so which $T$ would we put into the Clausius relation exactly? In fact, one could argue that because the temperature is changing, the occupation of the energy levels in the box is also changing, which must change the entropy. But because the temperature is going down, we are favoring lower energy states and there are fewer arrangements, so the entropy of the gas should actually be decreasing! (Presumably the entropy of the universe is increasing as the piston is moving, somehow). But this assumption is actually incorrect. Rather, the population of all the levels is staying exactly the same, because there is no heat entering or leaving that can rearrange the occupancy of the levels. Rather, it is the decrease of the energy levels themselves (which depend inversely on the length) that causes the temperature to go down, not the re-arrangement of the occupation of these levels. So in fact the entropy remains constant, and $\Delta S = 0$ during this adiabatic process. This is in spite of the fact that the volume is three times larger, so in principle the particles can occupy three times more places in the box.

In any case, the system is very different from the case where the piston is jerked back suddenly.

2. (a) The two equations that we know we have to satisfy are

$$\sum_i p_i = 1 \quad \text{and} \quad \sum_i p_i \epsilon_i = \frac{U}{N}.$$ 

Note that the right hand side of the second equation is $U/N$ rather than $U$ because we are summing over the probabilities $p_i$ not the occupations $n_i$. The number of levels is $\alpha + 1$, so $\alpha$ is the upper limit on the sums above (the sum starts with $i = 0$). We are told that the probabilities of occupying all of the energy levels $\epsilon_1$ are the same, so the equations become

$$\sum_i p_i = p_0 + \alpha p_1 = 1 \quad \text{and} \quad \sum_i p_i \epsilon_i = p_0 \epsilon_0 + \alpha p_1 \epsilon_1 = \frac{U}{N}.$$ 

Let’s define the energy unit $u \equiv U/N \epsilon_1$; then $p_1 = u/\alpha$ and $p_0 = 1 - \alpha p_1 = 1 - u$.

(b) The entropy is therefore

$$S = -N k_B \sum_i p_i \ln(p_i) = -N k_B [p_0 \ln(p_0) + \alpha p_1 \ln(p_1)]$$

$$= -N k_B \left[ (1 - u) \ln(1 - u) + u \ln \left( \frac{u}{\alpha} \right) \right],$$

where again there are $\alpha$ terms involving $p_1$.

(c) Let’s use the fundamental formula for the microcanonical ensemble:

$$\frac{1}{T} = \frac{\partial S}{\partial U} = \frac{\partial S}{\partial u} \frac{\partial u}{\partial U} = \frac{1}{N \epsilon_1} \frac{\partial S}{\partial u}$$

$$= \frac{1}{N \epsilon_1} (-N k_B) \left[ -\ln(1 - u) - 1 + \ln \left( \frac{u}{\alpha} \right) + 1 \right] = -\frac{k_B}{\epsilon_1} \ln \left( \frac{u}{\alpha(1 - u)} \right) = \frac{k_B}{\epsilon_1} \ln \left( \frac{\alpha(1 - u)}{u} \right).$$

So the constitutive relation connecting temperature and energy is

$$\ln \left( \frac{\alpha(N \epsilon_1 - U)}{U} \right) = \frac{\epsilon_1}{k_B T}.$$
In principle, this is all that this question is asking for. But in practice, we can solve for $u$:

$$\frac{\alpha(1-u)}{u} = \exp\left(\frac{\epsilon_1}{k_BT}\right).$$

I can express the exponential as $\gamma \equiv e^{\epsilon_1/k_BT}$ so that $\alpha - \alpha u = \gamma u$, which gives $u = \alpha/(\alpha + \gamma)$, or

$$u = \frac{U}{N\epsilon_1} = \frac{1}{1 + e^{\epsilon_1/k_BT}/\alpha}.$$

The probabilities are therefore

$$p_0 = 1 - u = 1 - \frac{1}{1 + e^{\epsilon_1/k_BT}/\alpha} = 1 + e^{\epsilon_1/k_BT}/\alpha - 1 = \frac{1}{\alpha e^{-\epsilon_1/k_BT} + 1}; \quad p_1 = \frac{u}{\alpha} = \frac{1}{\alpha + e^{\epsilon_1/k_BT}}.$$

(d) First let’s see what happens at low temperatures when I do use my explicit formulas. If $k_BT \ll \epsilon_1$ then $p_0 \to 1$ and $p_1 \to 1/e^{\epsilon_1/k_BT} = e^{-\epsilon_1/k_BT} \to 0$. Thus, all of the particles will be found in the ground state. The rescaled mean energy likewise goes to $\alpha \to 0$. Thus, all of the particles will be found in the ground state.

Suppose now that I didn’t solve for $u$ explicitly. Then I have to use the constitutive equation; for $k_BT \to 0$, the right hand side diverges. This can only happen if $u \to 0$. (Note that $u \to -\infty$, i.e. making the numerator very large rather than the denominator very small) is not allowed because $u + 1 \to u$ for large $u$. If $u \to 0$ then $p_0 \to 1$ and $p_1 \to 0$, as expected. In either case, these results are completely intuitive: all of the particles are found in the ground state as $T \to 0$.

(e) In the limit of very high temperature, we can again use the explicit formulas. The argument of the exponential becomes very small and so we can take a Taylor series; the rescaled mean energy then becomes

$$u \approx \frac{1}{1 + \frac{1}{\alpha}\left(1 + \frac{\epsilon_1}{k_BT}\right)} \approx \frac{1}{1 + \frac{1}{\alpha}} = \frac{\alpha}{1 + \alpha}.$$

The probabilities are then

$$p_0 = 1 - u = 1 - \frac{\alpha}{1 + \alpha} = \frac{1 + \alpha - \alpha}{1 + \alpha} = \frac{1}{1 + \alpha} \quad \text{and} \quad p_1 = \frac{u}{\alpha} = \frac{1}{1 + \alpha}.$$

In other words, the probabilities of occupying any of the levels is equal, and equal to one over the total number of levels $1 + \alpha$. This is exactly what we would expect in the classical limit (at high temperature).

The other way to obtain this, without explicitly solving for $u$ first, is to use the fact that we know that the classical (high-temperature) limit is the one where all of the probabilities are equal, so that $p_0 = p_1$. This means that $1 - u = u/\alpha$ or $u(1 + 1/\alpha) = u(\alpha + 1)/\alpha = 1$. So we have $u = \alpha/(\alpha + 1)$, just as we found by solving for everything explicitly. We can now substitute back in to find the probabilities, and of course the results are exactly the same as above.