First 176 Midterm Exam: Answers

Professor Greenside

Wednesday, February 18

A reminder for future quizzes and exams: work on those problems first that are worth the most points. The true false and multiple choice questions can be interesting to think about but reward you with few points compared to the problems that require writing out some answer.

True or False Questions (2 points each)

For each of the following statements, please circle **T** or **F** to indicate whether a given statement is true or false respectively.

1. **T / F** For an ideal gas, the ratio of the specific heats C_P/C_V is equal to the adiabatic exponent γ.

   Answer: T This problem required a short calculation. From the ideal gas law in the form $V = NkT/P$ and from the formulas $U = Nf(kT/2)$, $C_v = (\partial U/\partial T)_V = Nfk/2$, and $C_P = (\partial U/\partial T)_P + P(\partial V/\partial T)_P$ given at the beginning of the midterm, you can calculate that:

$$\begin{aligned} C_p &= (\partial U/\partial T)_P + P(\partial V/\partial T)_P && (1)\\ &= (Nfk/2) + P\,(Nk/P) && (2)\\ &= (f/2+1)\,Nk && (3)\\ &= (f+2)Nk/2 && (4)\\ &= \frac{(f+2)}{f}\left(fN\frac{k}{2}\right) && (5)\\ &= \gamma C_V, && (6)\end{aligned}$$

   so the statement is true.

2. **T / F** It is possible for the heat capacity C_P of a substance to be infinite at a finite temperature.

   Answer: T This was mentioned briefly in Schroeder in the discussion of specific heats. From the definition Eq. (1.4) on page 28, $C = Q/\Delta T$, we can see that the specific heat could be infinite if it is possible to add heat to a system (positive numerator) without changing its temperature (zero denominator). But this is exactly what happens during some phase transitions such as the melting of ice or the boiling of water[1]. Looking for a sharp peak in the specific heat (experimentally or computationally in a simulation) is also a way to *discover* a phase transition in some novel substance or in some novel regime: a careful measurement (say carried out during a computer-controlled experiment) of the substance's specific heat as a function of temperature might reveal a large peak, suggesting a phase transition.

3. **T / F** When a closed path is traced out in the PV-plane of an ideal gas, starting at some point A on the path and returning back to A, the total amount of heat absorbed by the gas will depend on the position of the starting point A on the path.

   Note: for this problem, assume that the total work done on the gas after following the path from A back to A is nonzero.

---

[1] I say "some" phase transitions because there are phase transitions of a different kind than the melting of a solid or the vaporization of a liquid, say the loss of ferromagnetism as a magnet is heated above a certain temperature, for which the temperature does not stay constant during the transition.

Answer: F This is a qualitative question that you can settle by drawing some representative closed loop, e.g., a circle, in the PV-plane of an ideal gas. If you start at different points on the closed curve and trace all the way around back to the same points, you should be able to convince yourself that you always end up going once around the entire area enclosed by the loop, which means that the total compression or extension work done (area enclosed by the curve) is always the same, no matter where you start. Since the total energy U doesn't change when you start at some point and return to that point in the PV plane, if the work stays the same, the heat that enters or leaves the system, which is the negative of the work, must also be the same.

4. **T / F** It is possible to trace a closed path in the PV-plane of an ideal gas such that the total heat absorbed and the total work done on the gas are both zero.

   Note: In your thinking, do not include the trivial case in which the gas goes from point A to point B on some path and then returns to A by traveling backwards along the same path, i.e. assume that the closed path encloses a finite area.

   Answer: T A closed curve that crosses itself one or more times, like the infinity symbol ∞, is an example of a curve for which the total work done is zero and so the total heat is also zero. All you need to arrange is for the two closed loops each to contain the same area: then tracing one loop will enclose the negative of the area enclosed by the other loop, canceling to zero.

5. **T / F** In an Einstein solid of N identical harmonic oscillators, increasing the number of energy units q corresponds to increasing the temperature T of the solid.

   Answer: T This was a general knowledge question, that was implied but never quite stated directly by Schroeder. The bound states of quantum mechanical systems have discete energy levels and the energy of the system is determined by which energy levels are "occupied", i.e. have an energy unit associated with them. Adding heat to a macroscopic system like an Einstein solid, which will increase its temperature since there is no phase transition in an Einstein solid (at least none that we have discussed or mentioned), necessarily corresponds to adding energy units to the oscillators which means increasing the number of energy units q.

   In Chapter 3, page 91, we will soon show how to calculate the temperature of an Einstein solid through the definition $1/T = (\partial S/\partial E)_{N,V}$ and by using our ability to calculate the multiplicity Ω and so the entropy $S = k \ln \Omega$.

6. **T / F** A careful experimental measurement over one hour of the temperature T of some equilibrium macroscopic solid whose width is $0.1\,\mathrm{m}$ will include the effects of all the possible microstates of the solid.

   Answer: F This point was made several times in Schroeder: a macroscopic system with Avogadro's number of components will have a very large number of microstates (i.e. the exponential of a large number such as $\exp(10^{23})$. This number of microstates is so huge that even an experiment lasting the age of the universe will only sample an infinitesimal fraction of the total number of microstates. This does not imply the breakdown of thermodynamics or of science since, for macroscopic systems, the multiplicity is so sharply peaked about the state corresponding to thermodynamic equilibrium that most of the very few microstates sampled will correspond to thermodynamic equilibrium.

7. **T / F** If an isolated Einstein solid is in thermodynamic equilibrium and has N_A oscillators in one subsystem and N_B oscillators in the other subsystem with $N_A \neq N_B$, and if the entire solid has q units of energy, then the most likely amount of energy to be observed in system A is $q\,N_A/(N_A+N_B)$. (Here the integers N_A, N_B, and q are all large numbers.)

   Answer: T We learned in Chapter 2 that, because of the extremely narrow peak in the multiplicity Ω of accessible states in an equilibrium macroscopic system, it is overwhelmingly likely to observe an equilibrium system with those values of its macroscopic parameters that correspond to the most likely macrostate. For two Einstein solids that are weakly interacting, one would guess correctly that a given total amount of energy q (more precisely qhf where h is Planck's constant and f is the oscillator frequency) would, in equilibrium, be distributed in proportion to the number of oscillators in each solid. Thus a fraction $N_A/(N_A + N_B)$ of the energy will end up in solid A and $N_b/(N_a + N_b)$ will end up in solid B, with these two fractions adding up to one.

This point was made indirectly on pages 58-59 of Schroeder, especially Figure 2.5 on page 59. Here he considered two solids with unequal numbers of oscillators, $N_A = 300$ and $N_B = 200$. The energy q_A that gives the maximum value of the multiplicity function $\Omega(q_A) = \Omega_A \Omega_B$ corresponds to $(300/(300 + 200)) = 0.6 q_{\text{total}} = 60$ units.

8. **T / F** If an isolated Einstein solid has two subsystems with equal number of oscillators $N_A = N_B = N \gg 1$, and if the solid has an amount of energy units $q > N$, and if at a particular moment all of the energy q is observed to be in subsystem A, then you can conclude that the solid is not in thermodynamic equilibrium.

   Answer: F Strictly speaking, you can not tell by observing a particular accessible microstate of some system whether that system is in thermodynamic equilibrium since the system may be in thermodynamic equilibrium and you just happened to observe one of the rare microstates that represents a non-equilibrium distribution of energy. But practically speaking, the probability of observing any microstate of a macroscopic system whose macroscopic parameter (say energy) does not correspond to the few microstates with the largest multiplicity is a tiny number (the reciprocal of a very large number), it would be similar to throwing 10^{23} pennies and finding that they all come up heads. So if you were to observe all of the energy in one macroscopic subsystem during some experiment, your first conclusion would be that something else is going on, e.g. there is a bias in the experiment, perhaps some unknown mechanism that is transfering heat from subsystem B to subsystem A, or that is preventing heat from A diffusing to B.

9. **T / F** For n a large integer and $\alpha > 1$ some real number, the sum of the n powers $1^\alpha + 2^\alpha + \ldots + n^\alpha$ is approximately equal to $(\alpha/2) n^{\alpha+1}$.

   Answer: F This question was intended to see if you understood the spirit of how the Stirling approximation was obtained, which was to approximate the finite sum $\ln(1) + \ln(2) + \ldots + \ln(n)$, which one can think of as the sum of adjacent block-like areas $\ln(1) \times 1 + \ln(2) \times 1 + \ldots$ of height $\ln(i)$ and base 1, by the integral $\int_1^n \ln(x)\, dx$. The idea is general and leads to approximations for any sum of some function $f(x)$ over the integers 1, 2, …, n. Here the function $f(x) = x^\alpha$ so

$$1^\alpha + \ldots + n^\alpha \approx \int_1^n x^\alpha \, dx = \frac{1}{\alpha+1}\left(n^{\alpha+1} - 1\right) \approx \frac{n^{\alpha+1}}{\alpha+1}, \tag{7}$$

   where in the last step I used the fact that, for $\alpha > 1$ and n large, the expression $n^{\alpha+1} \gg 1$ so the 1 can be dropped inside the parentheses. I encourage you to explore with Mathematica how well this approximation works for several values of α and of n.

Multiple Choice Questions (4 points each)

Circle the letter that best answers each of the following questions.

1. A large solid block of metal has unequal dimensions $L_x \times L_y \times L_z$ such that $L_x > L_y > L_z$. If the thermal diffusivity of the block is κ, then the least amount of time that an experimentalist should wait for the block to be close to equilibrium is

   (a) L_x^2/κ (b) L_y^2/κ (c) L_z^2/κ (d) L_x/κ (e) L_y/κ (f) L_z/κ

Answer: (a) or (c) This turned out not to be a well stated problem and I will also accept (c) for an answer. (So please get in touch with me if you want four points back if you chose (c)). The reason the problem is not well stated is that the answer depends on the context of how the block is allowed to reach equilibrium.

Answer (a) would be appropriate if the block was thermally insulated from the rest of the world (which is what I had in mind but unfortunately did not state). In this case, if the block had a non-uniform temperature, with some parts hotter and some parts colder, an experimentalist would have to wait for heat to diffuse (smear out) along the longest dimension L_x of the block for equilibrium to be attained, i.e. one would have to wait at least some integer multiple of the relaxation time L_x^2/κ to have some confidence that the block was close to equilibrium.

But if the block is not isolated but is instead immersed in some well stirred isothermal environment, say in a tub of water that has a temperature controller and some fan or pump to mix the water rapidly, then all surfaces of the block will be exposed to the same constant temperature and so the block will reach thermodynamic equilibrium on a time scale that is some integer multiple of L_z^2/κ, based on the shortest dimension L_z, since every part of the block is within a distance $L_z/2$ of the surface.

The isothermal environment has to be well stirred because if you suspend the block in, say a tub of water that is not stirred, the water in contact with the surface of the block will develop its own nonuniform temperature distribution because of its contact with the presumably different temperature of the block, and then the time scale for the block to reach equilibrium will be at least L_z^2/κ since the non-uniform temperature difference in the water would have to diffuse across the longest length of the block for equilibration to take place.

2. Two identical bubbles A and B of an ideal gas form at the bottom of a lake and then rise upwards toward the lake's surface. Because the water pressure decreases from the bottom to the surface, both bubbles expand as they rise. However, bubble A rises so quickly that there is no time for heat to flow into or out of the bubble, while bubble B rises so slowly (say it is transported by a lazy water spider) that its temperature always stays the same (the surrounding water is isothermal). When both bubbles are just below the lake's surface

   (a) they will have the same diameter.

   (b) bubble A will be the larger bubble.

   (c) bubble A will be the smaller bubble.

Answer: (c)

This was Problem 1.38 on page 26 of Schroeder and a good conceptual question. The key insight is that, when both bubbles are just below the surface of the lake, they have the same pressure P (since they are at the same depth of water and the local pressure is determined by the water depth) and they have the same number of particles N (since the bubbles started off identically and there is no information that addresses whether air is lost or gained from the surrounding water so the only reasonable assumption is that N is conserved). From the ideal gas equation $PV = NkT$ in the form $V = V(T) = (Nk/P)T$, we see that the final volume V of the bubble will depend on the final temperature T of the bubble, with the colder bubble having the smaller volume.

We are told that bubble A rises so rapidly that no heat enters or leaves the bubble, i.e. this is an adiabatic bubble. Conservation of energy $\Delta U = Q + W = W$ with $Q = 0$ then tells us that the internal energy $U = Nf(kT/2)$ of the gas in the adiabatic bubble is determined by the work W done by the bubble. Since the bubble expands as it rises (decreasing pressure), it does expansion work against the surrounding water, which means that $W = \Delta U < 0$, which means that the temperature inside the bubble must decrease from its original value, which is the temperature of the surrounding water. In contrast, the bubble carried by the water spider is isothermal since it rises so slowly that it has time to fully equilibrate with the surrounding water. Thus bubble A arrives near the surface of the lake with a decreased temperature compared to bubble B and therefore has the smaller volume, hence (c).

Note: I was not trying to be funny about the water spider. There are spiders that spend much of their lives underwater and that do transport small bubbles under the water. These spiders build a dome-like web under the water that can trap air and then fill the dome with air that they capture above the surface as tiny bubbles with hairs in their abdomen. As to why I know about water spiders, I went through a "spider phase" when I was about ten and for a few years kept a sizable collection of living spiders of different New England species in the basement of my home.

3. For x a sufficiently small number, the expression

$$\ln\left[\frac{1-\ln\big(1-\ln(1-x)\big)}{1+\ln\big(1+\ln(1+x)\big)}\right]$$

is approximately equal to

(a) 0 (b) $2x$ (c) $-2x$ (d) x^2 (e) $-x^2$

Answer: (c) This is a problem that required multiple applications of the lowest-order approximation $\ln(1+x) \approx x$ for x small, that you learned to use when simplifying the log of a multiplicity, $\ln\Omega$, e.g., for an Einstein oscillator for which $q \gg N \gg 1$. The above expression can be simplified as follows, starting with the innermost log expressions:

$$\begin{aligned}
\ln\left[\frac{1-\ln\big(1-\ln(1-x)\big)}{1+\ln\big(1+\ln(1+x)\big)}\right] &\approx \ln\left[\frac{1-\ln\big(1-(-x)\big)}{1+\ln\big(1+(x)\big)}\right] && (8)\\
&= \ln\left[\frac{1-\ln(1+x)}{1+\ln(1+x)}\right] && (9)\\
&\approx \ln\left[\frac{1-x}{1+x}\right] && (10)\\
&= \ln(1-x)-\ln(1+x) && (11)\\
&\approx (-x)-(x) = -2x. && (12)
\end{aligned}$$

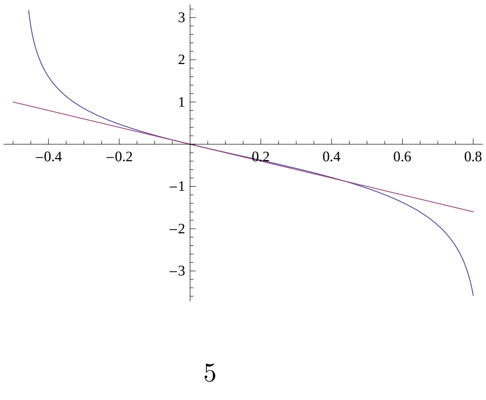
One could have also simplified the expression $\ln[(1-x)/(1+x)]$ like this:

$$\ln\left[\frac{1-x}{1+x}\right] \approx \ln\left[(1-x)\times(1-x)\right] \approx \ln\left[1-2x\right] \approx -2x, \tag{13}$$

using the facts that $1/(1+x) \approx 1-x$ and $(1-x)^2 = 1-2x+x^2 \approx 1-2x$ to lowest order in the small quantity x. Some students got as far as $\ln(1-x)-\ln(1+x)$ and then unfortunately made a sign error, getting zero instead of $-2x$.

Note however that the lowest order approximation to the similar expression $\ln(1+x)+\ln(1-x)$ is not $x-x=0$ but $\ln((1+x)(1-x)) = \ln(1-x^2) \approx -x^2$, you have to go to second-order to see the first non-zero power of x. Alternatively, there are times when you have to use the second-order approximation $\ln(1+x) \approx x - x^2/2$.

Using Mathematica, we can see that the lowest-order approximation $-2x$ gives a good approximation of this complicated function over a rather substantial range of x, $[-0.15, 0.5]$:



4. A long thermally isolated plastic cylinder is divided into two equal halves by a thin circular metallic impermeable partition that has an extremely small mass and that can easily slide back and forth along the axis of the cylinder with negligible friction. One half of the cylinder is filled with He gas and the other half with gaseous sulfur hexafluoride SF_6 (the ratio of the molecular masses is $(32 + 6 \cdot 19)/4 = 146/4 \approx 37$) so that thermodynamic equilibrium is attained with constant pressures, temperatures, and volumes on both sides of the partition. An electrical current is then passed through the partition so that its temperature instantly increases by a large amount. Immediately after this temperature increase and before the temperatures of the two gases can change, the piston will

   (a) not move at all.

   (b) move a tiny bit so as to decrease the volume of He gas.

   (c) move a tiny bit so as to increase the volume of He gas.

Answer: (a)

This problem was motivated by a PRS problem that we discussed in class: if an ideal gas of temperature T was inside a container whose walls were suddenly increased to a temperature $T' > T$, would the pressure on the walls change over a short period of time? If you remember, the answer was "yes" because molecules coming in contact with the hotter wall on average came away from the wall with an increased speed, and so the momentum transfer $\Delta p_x = m\Delta v_x$ (assume that x is the coordinate perpendicular to the wall) that is the origin of the pressure, was temporarily greater since the return momentum mv', which has an opposite sign to mv, had an increased value. This PRS problem also partially explained why radiometers rotate: the black side of the radiometer fin heats up compared to the white side (black absorbs more light energy), and air molecules striking the black side come away with an increased speed so there is an increased pressure on the black side of each fin.

This problem is a variation of the radiometer problem in which two different gases are both initially in equilibrium with some movable partition and then the partition is increased in temperature. It is clear that the momentum transfer will increase for both gases, but will one gas end up briefly producing a greater pressure than the other gas, causing the partition to move?

One can answer this question by *first* considering the details of the momentum transfer of a single molecule. For simplicity, let's assume that the surface of the partition is perpendicular to the x coordinate and that molecules move only along the x coordinate, and let's consider a gas molecule of mass m with initial x-velocity component v_x that is about to strike the hot partition. Since the gas is in thermodynamic equilibrium, we can assume equipartition and so

$$\frac{1}{2}mv_x^2 = \frac{1}{2}kT \qquad \text{or} \qquad v_x = \sqrt{\frac{kT}{m}}, \tag{14}$$

where T is the temperature of the gas. The incoming or initial momentum is then

$$p_i = mv_x = \sqrt{mkT}. \tag{15}$$

After the particle reflects off the hot partition with temperature T', we can guess for simplicity that its new speed on average will be $v_x' = \sqrt{kT'/m}$, corresponding to being in thermal equilibrium with the hot partition. The outgoing or final momentum will then be

$$p_f = -mv_x' = -\sqrt{mkT'}, \tag{16}$$

where there is a minus sign since we assume the particle has reversed direction along the x coordinate. The total change in momentum therefore has magnitude

$$|\Delta p| = |p_f - p_i| = \sqrt{mkT} + \sqrt{mkT'} = \sqrt{mk}\left(\sqrt{T} + \sqrt{T'}\right). \tag{17}$$

Based on a single particle, we would incorrectly conclude that the answer should be (b) since, indeed, the more massive the particle, the bigger the momentum change since Eq. (17) says that $\Delta p \propto \sqrt{m}$, so the more massive sulfur hexafluoride molecules should win, pushing the partition into the He gas and shrinking the volume of He.

But as we have learned this semester, the pressure is not just due to the momentum change per particle, it has to include the rate at which the particles arrive at the wall. Because of equipartition, more massive particles move more slowly than less massive particles which means they arrive at the wall less frequently and this might compensate for the increased momentum change per particle. We can work out the details using the simplest and quickest version of the kinetic theory to explore the situation.

So let's consider a small area A on the wall, in which case all particles within the cylinder $(v_x \Delta t)A$ will collide with the wall within a time interval Δt and the number of such particles is $[(v_x \Delta t)A]\,(N/V)$, where the ratio N/V does not change with the temperature of the partition. The pressure P due to the gas is then the total number of particles hitting the wall per unit time per unit area times Eq. (17), the momentum transfer Δp per particle:

$$\begin{aligned} P &\approx \frac{1}{\Delta t A}\left((v_x \Delta t A) \left(\frac{N}{V}\right) \times \Delta p \right) && (18) \\ &= \left(\frac{N}{V}\right) v_x \Delta p && (19) \\ &= \left(\frac{N}{V}\right) \sqrt{\frac{kT}{m}}\, \sqrt{mk} \left(\sqrt{T} + \sqrt{T'} \right) && (20) \\ &= \left(\frac{Nk}{V}\right) \left(T + \sqrt{TT'} \right). && (21) \end{aligned}$$

You can see that the mass of the particle has canceled out and so the pressure change is independent of the particle mass, so the answer is (a).

Note that it was not worth doing a careful calculation to get an accurate numerical prefactor, say for an isotropic gas, because all we needed to determine was that the mass canceled out of the expression.

Problems That Require Writing

Please write your answers to the following problems on extra blank sheets of paper. Also make sure to write your name and the problem number at the top of each sheet. In this part of the exam, you need to justify all of your answers to get full credit.

1. (8 points) Using Stirling's approximation, derive an approximation for the multiplicity of an Einstein solid in the low temperature limit for which the number N of oscillators and the amount q of energy satisfy $N \gg q \gg 1$. To obtain a simple final expression, ignore large numbers that multiply very large numbers.

   Answer:

   $$\Omega \approx \left(\frac{eN}{q}\right)^q \qquad \text{for } q \ll N. \tag{22}$$

   A detailed derivation is already available to you on pages 63-64 of Schroeder: the problem is exactly identical provided that you simply switch the symbol q with the symbol N everywhere. In fact, if you remembered the expression $(eq/N)^N$ from Eq. (2.21) of Schroeder, and if you also observed that

   $$\binom{q+N-1}{q} \approx \binom{q+N}{q} = \frac{(q+N)!}{q!\,N!} = \frac{(N+q)!}{N!\,q!} = \binom{N+q}{N}, \tag{23}$$

   you could have written down the answer instantly without any work, by just swapping the symbols $q \to N$ and $N \to q$.

   I do observe here that too many students could not complete the algebra. Typically, people forgot to work with $\ln \Omega$ and people forgot to look for opportunities to simplify using the approximation $\ln(N +$

$q) \approx \ln(N) + q/N$. Some students didn't drop prefactors that were large numbers like $\sqrt{2\pi N}$, even though the problem suggested doing so, and some students threw the baby out with the bathwater, neglecting q compared to $q\ln(N/q)$ with the result that the e^q factor in the final answer, a very big number, disappeared from the expression.

2. (10 points) An isolated box of volume V is divided into two compartments, A and B. Compartment A contains N_A atoms of an ideal gas at temperature T_A in a volume V_A while compartment B contains N_B atoms of the same gas at a *higher* temperature $T_B > T_A$ in a volume V_B such that $V = V_A + V_B$. A thin immovable impermeable metal partition separates the two compartments.

   Using an appropriate argument supported with mathematical equations, use the second law of thermodynamics in the form $dS/dt > 0$ together with the definition of temperature $1/T = dS/dE$ to explain why heat necessarily flows from the hotter compartment to the cooler compartment. Make sure that you clearly indicate any assumptions that you have to make.

   Answer: I wrote out the details in the exams so don't give the full details here. This argument is extremely important for the course and you should fully understand and master it since the argument explains why temperatures are uniform throughout an equilibrium system *and* why energy flows from a high temperature system to a low temperature system.

   Simple changes of this argument, in which one treats the entropy $S = S(V)$ as a function of volume V for fixed energy and number of particles, or the entropy $S = S(N)$ as a function of the number of particles for fixed volume and fixed energy, leads to the conclusion that the quantity $\partial S/\partial E|_{E,N} = P/T$ must be constant throughout an equilibrium (maximum entropy) system which therefore implies that the pressure must be constant and uniform throughout an equilibrium system, or that the quantity $\partial S/\partial N|_{E,S} = -\mu/T$ must be constant and uniform throughout an equilibrium system, which implies that a quantity μ called the chemical potential must be constant throughout an equilibrium system.

   Briefly, the key steps of the solution involved first observing that the entropy $S(E) = S_A(E_A) + S_B(E_B)$ is additive over weakly interacting macroscopic subsystems A and B of some isolated system[2].The second law of thermodynamics in the form $dS/dt > 0$ for a nonequilibrium system (entropy increases over time) then implies by the chain rule for differentation:

$$\frac{dS}{dt} = \frac{dS_A}{dE_A}\frac{dE_A}{dt} + \frac{dS_B}{dE_B}\frac{dE_B}{dt} = \frac{dE_A}{dt}\left(\frac{dS_A}{dE_A} - \frac{dS_B}{dE_B}\right) = \frac{dE_A}{dt}\left(\frac{1}{T_A} - \frac{1}{T_B}\right) > 0. \tag{24}$$

   Here I have used the fact that energy is conserved in an isolated system so that

$$E = E_A + E_B = \text{constant} \quad \Rightarrow \quad \frac{dE_A}{dt} + \frac{dE_B}{dt} = 0. \tag{25}$$

   You can finish the argument from here, concluding that if $T_B > T_A$ then necessarily $dE_A/dt > 0$ so that the energy of system A increases while the energy of system B decreases. The energy keeps changing (moving from A to B) until $dS/dt = 0$ or $dS/dE_A = 0$ or when $dS_A/dE_A = dS_B/dE_B$, when equilibrium is attained and the temperatures of A and B are the same.

3. (6 points) Without using any mathematics, explain why the expression

$$\binom{\alpha_1 + \alpha_2 + \alpha_3 + \beta - 1}{\beta} = \sum_{\beta_1+\beta_2+\beta_3=\beta} \binom{\alpha_1 + \beta_1 - 1}{\beta_1}\binom{\alpha_2 + \beta_2 - 1}{\beta_2}\binom{\alpha_3 + \beta_3 - 1}{\beta_3},$$

   is a valid mathematical identity by interpreting this expression physically. The symbols α_i and β are nonnegative integers and the sum goes over all possible nonnegative integer values of the β_i that sum to β.

---

[2] The fact that the subsystems are macroscopic, i.e., that the number of molecules near their surfaces is a tiny fraction of the total number of molecules, is a key reason why interacting subsystems tend to be weakly interacting.

Answer: I corrected this problem in some detail in your exams so do not repeat the full argument here. What I was looked for in your answer were several key phrases:

(a) That this equation described three weakly interacting Einstein solids that can exchange energy with one another. The assumption of weakly interating is necessary to conclude that the multiplicity of the three systems at any particular moment in time (before they can reach thermodynamic equilibrium) is the product of the individual multiplicities.

(b) That the three solids together form a thermally isolated system, which implies energy conservation in the form $\beta = \beta_1 + \beta_2 + \beta_3$, where you needed to realize that the betas corresponded to Schroeder's notation of q, namely number of energy units hf in the oscillators of the Einstein solids.

(c) That the sum over all possible microstates of the three interacting Einstein solids (the right side of this identity), for all possible macroscopic values of their energies that are consistent with the total conserved amount of energy β, must equal the total number of microstates obtained by treating all three solids as a single solid with total number of oscillators $\alpha_1 + \alpha_2 + \alpha_3$ and with total energy β.

I will let the mathematically inclined members of the class see if they can find a way to prove this identity directly as a mathematical truth (induction is likely a good strategy). For the empiricists in the class, you can verify the truth of this statement by executing the following Mathematica code, which calculates the left side minus the right side and so should be zero for any choices of the nonnegative numbers of oscillators in each solid and for various choices of the nonnegative total energy:

```
fn[ a1_, a2_, a3_, b_ ] :=
  Binomial[ a1 + a2 + a3 + b - 1, b ]   (* left side *)
    - Sum[                              (* right side *)
         Sum[
            Binomial[ a1 + b1 - 1 , b1 ]
            Binomial[ a2 + b2 - 1 , b2 ]
            Binomial[ a3 + b - b1 - b2 - 1, b - b1 -  b2 ],
           { b2, 0, b - b1 }  (* inner sum depends on index b1 of outer sum *)
         ] ,
         { b1, 0, b }
      ]
```

4. (10 points) Consider two identical cubic dice of the sort used in board games, with each die having the numbers 1 through 6 on its six surfaces. Assume the dice are fair in that each number has the same probability of appearing when tossed.

   Consider the two dice as a macroscopic system whose macrostate is characterized by the sum of the values that appear on the top most surfaces after throwing the two dice. With an appropriate table, determine all possible macrostates of the two dice, list all the possible microstates for each macrostate, and give the probabilities for observing each macrostate.

   Answer: All students in the class got this problem so no need to write up a solution here. I would make one short comment, which is that it was not useful to reduce the various fractions representing probabilities, it was better to keep all the numbers with the same denominator of 36 so one can compare the various probabilities more easily.

5. Consider a box of volume V that contains an ideal gas in thermodynamic equilibrium that consists of N identical molecules, each of mass m, each moving with speed v, and such that the molecular velocities are isotropic. The gas is initially at temperature T with pressure P. A small flat metallic square of area A is attached to the inside surface of the box so that the square lies flush with the wall and such that the square is cooled to such a low temperature (by external machinery) that any gas molecules that come in contact with the square permanently stick.

(a) (10 points) In terms of the variables m, P, T, and A (but not in terms of v, N, or V), derive a formula for the amount of the heat per unit time that must be removed from the metal square in order to keep its temperature constant and cold. (Please make sure to use some brief phrases that explain key details or assumptions in your derivation.)

Answer:

$$\frac{dQ}{dt} = \frac{3}{8} AP \left(\frac{3kT}{m} \right)^{1/2} = \left(\frac{3}{4} \right)^{3/2} AP \left(\frac{kT}{m} \right)^{1/2} . \tag{26}$$

This problem was intended to be a minor variation of a problem that you have explored several times in recent homeworks, namely effusion of particles in an ideal gas (also photons) through some small hole in the wall. But somehow either many members of the class did not remember what they did in the homeworks or the wording of the problem threw students off because a surprisingly large number of students struggled with this problem. In particular, many students did not remember what the word "isotropic" meant, which was that the molecular velocities point in all possible directions with equal likelihood, which in turn implied that you needed to carry out some kind of multiple integral in spherical coordinates to add up all the contributions of molecules arriving at the metal plate from all possible directions inside the box. A gas whose molecules are not isotropic would be called "anisotropic", which would describe the simpler kinetic model in which all velocities are parallel to the Cartesian axes, with $1/6$ of the molecules moving in any particular direction.

(For future quizzes and exams: if you don't know the meaning of a possibly crucial word, please ask!)

Roughly, all that was needed here was to multiply the formula for flux of particles (number of particles hitting some area per unit time) associated with effusion with the kinetic energy per particle, $(1/2)mv^2$, which then gives the total amount of energy being received by a small cold plate of area A. You also had to use equipartition to eliminate the rms speed v in terms of the temperature of the gas.

Let me give the intended solution first, then discuss some other ways that one could approach this problem (and which some students used in their answers). Let's place a spherical coordinate system at the center of the small metal square, with the z or θ axis perpendicular to the surface of the square and pointing into the box. The total energy that the plate receives per unit time can be calculated as the total number of particles arriving at the plate per unit time times the energy per particle. The calculation is much simplified by the assumption that the speeds v are all the same; this is not true for a real ideal gas, for which the speeds obey a Maxwell-Boltzmann distribution $f(v)$ that we will derive and discuss later in the semester.

If we consider some small fixed interval of time Δt, then only those particles that are within a distance $v\Delta t$ of the area will hit the plate within time Δt. (We assume that the time is short enough that the hemisphere of radius $v\Delta t$ centered on A lies entirely inside the box.) Consider some small infinitesimal volume $dV = r^2 \sin(\theta)\, dr\, d\theta\, d\phi$ that is centered on the point with spherical coordinates (r, θ, ϕ) with $0 \le r \le v\Delta t$. The number of particles inside this infinitesimal volume is $dV \times (N/V)$ and the fraction of these particles actually moving toward the plate is the ratio $A\cos(\theta)/(4\pi r^2)$ given by the effective area of the plate, $A\cos(\theta)$, as projected onto the line of sight from the volume dV, compared to the entire surface area $4\pi r^2$ of a sphere centered on the volume dV. (This is specifically where the assumption of "isotropic" is used, the fraction of particles reaching a certain area on the surface of the sphere is just the ratio of that area to the sphere's surface area). Each particle in the volume dV that strikes the plate will deliver its total kinetic energy $(1/2)mv^2$ to the plate.

So the total amount of energy ΔQ that is delivered to a plate of area A (doesn't matter what the shape of the area is, circle or square or ellipse, so long as the area is small) within a time interval Δt is obtained by adding up the contributions from all the infinitesimal volumes dV within a distance $v\Delta t$ of the plate. This leads to the following triple integral:

$$\Delta Q = \int_0^{v\Delta t} dr \int_0^{\pi/2} d\theta \int_0^{2\pi} d\phi \left[\left(r^2 \sin(\theta) \times \frac{N}{V} \right) \times \frac{A\cos(\theta)}{4\pi r^2} \right] \times \frac{1}{2} mv^2 . \tag{27}$$

Note how the variable θ varies over only half of its possible range, $0 \leq \theta \leq \pi/2$, since only infinitesimal volumes inside the box can be included.

Note also how Eq. (27) is the same expression we discussed in class for the effusion of isotropic particles through some small hole of area A, but with the energy per particle added in as a factor. If we wanted instead the answer to some other transport problem, say the total mass, or the total electrical charge, or the total angular momentum delivered to the plate, all we have to do is replace the expression $(1/2)mv^2$ in Eq. (27) with the appropriate quantity.

Also note that my wording of the problem is not quite consistent. The problem mentions molecules, not atoms, which means that there is the possibility of rotational and vibrational thermal energy associated with each molecule, in addition to motion of the center of mass. To add up the total energy delivered to the plate by each molecule, I should replace $(1/2)mv^2$ in Eq. (27), which is correct for a monoatomic gas like He, with the expression $f(kT/2)$, where f would be 5, not 3, for air at room temperature consisting mainly of diatomic nitrogen. I'll let you work out the necessary change in the final answer.

The above triple integral is easily evaluated: the integral over ϕ gives immediately 2π since the integrand does not depend on ϕ, the integral over radius gives immediately $v\Delta t$ since the two r^2 terms in the integrand cancel, leaving no radial dependence in the integrand, and the integral over θ was given to you in the list of data at the beginning of the exam. Equation (27) then becomes (after dividing both sides by Δt):

$$\frac{\Delta Q}{\Delta t} = \frac{1}{8} m v^3 A \left(\frac{N}{V} \right). \tag{28}$$

This expression is inconvenient to use since the speed v is not as easily measured as pressure or temperature. So we can use equipartition:

$$\frac{1}{2} m v^2 = \frac{3}{2} kT \qquad \text{or} \qquad v^3 = \left(\frac{3kT}{m} \right)^{3/2}. \tag{29}$$

to eliminate v in terms of T. We can also eliminate the number density N/V in terms of the pressure by using the ideal gas law in the form:

$$\frac{N}{V} = \frac{P}{kT}. \tag{30}$$

Substituting Eq. (14) and Eq. (30) into Eq. (28) and simplifying leads to the desired answer, Eq. (26) above.

If you didn't remember what isotropic meant or how to set up the above triple integrals, I gave you most of the credit if you used the simpler but less accurate assumption that the molecular velocities are all parallel to the Cartesian coordinate axes so that only 1/6 of the molecules are moving toward the plate in a perpendicular cylinder of volume $(v\Delta t)A$. Many students even didn't remember this possibility and got an approximate answer by using what they remembered from the effusion homework problem, Problem 1.22 on page 14 of Schroeder, in which the average pressure $\overline{P}$ due to a single molecule of mass m colliding with a wall

$$\overline{P} = \frac{1}{A} \times m \overline{\left(\frac{\Delta v_x}{\Delta t} \right)}, \tag{31}$$

leads to an expression for N independent molecules colliding with a wall and bouncing elastically with $\Delta v_x = 2v_x$, giving

$$\overline{P} = \frac{m(2v_x)N}{A\Delta t}, \tag{32}$$

which can be solved for the number of particles arriving per unit time:

$$\frac{N}{\Delta t} = \frac{AP}{2mv_x}. \tag{33}$$

This could then be multiplied by the kinetic energy per particle, $(1/2)mv_x^2$, to get the expression

$$\frac{\Delta Q}{\Delta t} = \frac{AP}{2mv_x} \times \frac{1}{2} m v_x^2 = \frac{1}{4} A P v_x = \frac{1}{4} AP \left(\frac{kT}{m}\right)^{1/2}, \tag{34}$$

which has the same combination of parameters as Eq. (26) but a different numerical prefactor. This expression is fine for estimating order of magnitudes (like that requested for part (b)) but this approach didn't give you a chance to show off all the fancy knowledge you learned in working with an isotropic gas in spherical coordinates.

Finally, what if you didn't remember anything we discussed in class or in Schroeder? You could still deduce the form of the formula, good enough for order-of-magnitude estimates, by using *dimensional analysis*. The wording of the problem suggests that the answer must depend on the variables m, P, A, and T, and we can ask: what algebraic combination of powers of these variables

$$A\, m^{\alpha}\, P^{\beta}\, T^{\gamma}, \tag{35}$$

will have the same physical units as the energy per unit time dQ/dt? (It is clear that the area must enter as the first power A^1 since the number of molecules striking the plate is proportional to its area.) Now energy has units of "force times distance" and force has units of "mass times acceleration" and acceleration has units of "distance over time squared". If we let the symbols M, L, and T denote units of mass, length, and time respectively, we conclude that the physical units of dQ/dt are (please verify this!):

$$\frac{dQ}{dt} = L^2\, M^1\, T^{-3}. \tag{36}$$

Before trying to deduce the powers in Eq. (35), we need to observe that the temperature T is dimensionless and so at first glance can be raised to any arbitrary power. But in nearly all problems in statistical physics, the temperature T only appears in formulas through the expression kT which does have physical units of energy. Eq. (35), with kT instead of T, has the physical units

$$A\, m^{\alpha}\, P^{\beta}\, (kT)^{\gamma} = L^2\, M^{\alpha} \left(\frac{M}{LT^2}\right)^{\beta} \left(\frac{ML^2}{T^2}\right)^{\gamma} = L^{2-\beta+2\gamma}\, M^{\alpha+\beta+\gamma}\, T^{-2\beta-2\gamma}. \tag{37}$$

Equating the right most side of Eq. (37) to the right side of expression Eq. (36) leads to three equations in three unknowns:

$$2 - \beta + 2\gamma = 2, \qquad \alpha + \beta + \gamma = 1, \qquad -2\beta - 2\gamma = -3, \tag{38}$$

which you can solve[3] to find the values

$$\alpha = -\frac{1}{2}, \qquad \beta = 1, \qquad \gamma = \frac{1}{2}. \tag{39}$$

which means that the answer must be:

$$\frac{dQ}{dt} = A\, m^{-1/2}\, P^1\, (kT)^{1/2} = AP \left(\frac{kT}{m}\right)^{1/2}. \tag{40}$$

This indeed recovers the correct combination of the parameters in Eq. (26), and is off by a factor of $(3/4)^{3/2} \approx 0.6$, not bad at all.

(b) (6 points) Using your formula, estimate to *one* significant digit the heat per unit time (in units of joules/second or J/s) that needs to be removed from a one-millimeter metal square if the square is attached to the inside of a one liter box containing diatomic nitrogen (molecular weight 28 g) at

---

[3] The first and third equations lead to two simple equations in the two unknowns β and γ: $-\beta + 2\gamma = 0$ and $\beta + \gamma = 3/2$, leading to $\beta = 1$ and $\gamma = 1/2$ and then $\alpha = 1$ can be deduced from the middle equation.

STP (standard temperature and pressure so $T \approx 290\,K$ and $P \approx 1.0 \times 10^5\,\mathrm{N/m^2}$). Also assume that the gas parameters have not yet had time to change significantly from their initial values.

Note: You will save time if you simplify your expression algebraically before substituting any numbers. Also round numbers to one digit before combining them.

Answer:

$$\frac{dQ}{dt} = \frac{3}{8} AP \left(\frac{3kT}{m} \right)^{1/2} \approx 20\,\frac{\mathrm{J}}{\mathrm{s}}. \tag{41}$$

This is actually a substantial macroscopic amount of energy per second for a small area and so somewhat of a surprising result.

If you had the right formula, this was easy to estimate provided that you remembered that the mass m in Eq. (41) (or in the similar expressions Eq. (34) or Eq. (40)) was the mass per molecule, not the mass per mole. So the mass to use in these expressions for diatomic nitrogen with molecular weight 28 g was:

$$m\,\frac{\mathrm{kg}}{\mathrm{molecule}} = \frac{\left(28\,\frac{\mathrm{g}}{\mathrm{mole}}\right) \times \left(10^{-3}\,\frac{\mathrm{kg}}{\mathrm{g}}\right)}{6.0 \times 10^{23}\,\frac{\mathrm{molecules}}{\mathrm{mole}}}. \tag{42}$$

But you do *not* want to evaluate this number separately (takes extra time, there is the possibility of unnecessary errors), just substitute the above expression into Eq. (26) and combine all the numerical terms in one effort. This is actually desirable: there are more opportunties to combine or cancel terms.

Some students also made an unfortunate error in converting a square millimeter to a square meter, $(1\,\mathrm{mm})^2 = (10^{-3}\,\mathrm{m})^2 = 10^{-6}\,\mathrm{m}^2$.

An estimate to one digit could then be found as follows:

$$\begin{aligned}
\frac{dQ}{dt} &= \frac{3}{8} AP \left(\frac{3kT}{m} \right)^{1/2} && (43)\\
&\approx \frac{3}{8} \times 10^{-6} \times 10^{5} \times \left(\frac{3 \times (1.4 \times 10^{-23}) \times 290}{28 \times 10^{-3}/(6.0 \times 10^{23})} \right)^{1/2} && (44)\\
&\approx \frac{3}{8} \times 10^{-1} \times \left(\frac{3 \times 1.4 \times 2.9 \times 6}{2.8} \times 10^{-23+2-1+3+23} \right)^{1/2} && (45)\\
&\approx \frac{3}{8} \times 10^{-1} \times \left(30 \times 10^{4}\right)^{1/2} && (46)\\
&\approx \frac{3}{8} \times 10^{-1} \times \left(5 \times 10^{2}\right) && (47)\\
&\approx \frac{15}{8} \times 10 \approx \frac{16}{8} \times 10 && (48)\\
&\approx 2 \times 10^{1} = 20\,\frac{\mathrm{J}}{\mathrm{s}}. && (49)
\end{aligned}$$

Using a calculator, the answer to two significant digits is 1.9×10^1, so the estimate is good. Note how in line (45), I first combined all the numerical factors together before rounding, in case I want to use a calculator later to get a more accurate answer. I then saw that the 2.9 in the numerator cancels the 2.8 in the denominator, and that $1.4 \times 6 = 2.8 \times 3 \approx 3 \times 3$ so the remaining numbers multiply to about 27 which rounds to 30. The square root of 30 is 5 to one digit.

(c) (6 points) Draw schematic curves of how the pressure P, temperature T, and number of particles N vary with time for this gas that is in steady contact with an small extremely cold metal square. (You need to justify, at least briefly, why you draw your particular curves.)

Answer: Since this problem is identical to effusion in nearly all details (particles striking the plate are removed from the gas at exactly the same rate as passing through a hole of equal area), you should have been able to state immediately that the number of particles $N(t)$ decays exponentially with time, just like you worked out in an earlier homework assignment.

What about how the temperature $T(t)$ and pressure $P(t)$ vary? **The temperature turns out to be constant** (a point that many students missed). This is because the molecules that strike and stick to the cold plate do not return to the gas, so that the molecules remaining in the gas continue to have the same speed v and so the same temperature via the equipartition result $(3/2)kT = (1/2)mv^2$.

Once you know that the temperature is constant, the ideal gas formula in the form $P = P(N) = (kT/V)N$ with T and V constant immmediately implies that P behaves the same way as N and also decays exponentially.

A challenge: the speeds of the molecules in an equilibrium gas are not all equal, most are close to $v_{\rm rsm}$ but some move slower, some move faster according to the Maxwell-Boltzmann distribution (see Fig 6.13 on page 245 of Schroeder). Will the temperature of a gas with a distribution of speeds also stay constant if the gas is exposed to a cold plate that traps all the particles? See if you can reason this out intuitively, before you learn how to calculate the answer in detail when we get to Chapter 6.