Quiz 4 for Physics 176: Answers

Professor Greenside Friday, March 22, 2009

True or False Questions (2 points each)

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

1. \mathbf{T} / \mathbf{F} A paramagnet in its lowest energy state (all N magnetic dipoles parallel to the external magnetic field B) has a negative temperature T.

Answer: F All substances reach their lowest possible energy state at absolute zero, T = 0, even a substance like a paramagnet that can have negative temperatures. You should remember that negative temperatures are hotter than the highest positive temperature in that a substance with a negative temperature will always transfer heat to a positive temperature substance. One way to think of a substance with a negative temperature is that they are unstable. Like balancing a marble on top of a sphere, such that any tiny perturbation will cause the marble to roll off, the negative temperature regime of the paramagnet corresponds to having magnetic dipoles pointing the "wrong" way, antiparallel to the fixed external magnetic field. These dipoles can release energy, and so transfer heat, by rotating parallel to the magnetic field.

Also keep in mind that negative temperatures only arise when the entropy decreases with increasing energy. This typically occurs when the total energy of a system is bounded. Thus for a paramagnet, there is a maximum possible energy, name $E = N\mu B$ in which all the spin-1/2 dipoles point antiparallel to the *B* field. As the energy increases toward its maximum value, the multiplicity Ω starts to decrease (e.g., there is only way way to arrange all the dipoles to point the wrong way), which means the entropy decreases with increasing *U*, which means the temperature $\partial S/\partial U$ must be negative.

2. **T** / **F** It is possible for the entropy of a system to increase after the system undergoes an adiabatic process (no heat into or out of the system).

Answer: T See Figure 3.16 on page 113 of Schroeder, the right panel of which shows a system that undergoes an adiabatic process, free expansion into a vacuum, which results in increase in entropy (because molecules can move around in a larger volume) without a transfer of heat.

3. **T** / **F** If two macroscopic systems A and B can exchange particles of the same type and together form an isolated system, and if the chemical potentials of these systems satisfy $\mu_A < \mu_B$, then particles will spontaneously move from system A to system B.

Answer: F See Figure 3.19 of Schroeder on page 116 and the relate discussion. The chemical potential is similar to the temperature in that particles spontaneously move toward regions of lower chemical potential, just as heat spontaneously moves to lower-temperature regions of a system. Generally, chemical potentials increase with increasing concentration of some object of interest (say atoms or molecules), so a difference in chemical potential between two parts of a system usually corresponds to a difference in concentration. Most of you would accept that molecules "flow down a gradient", i.e. it is most likely for atoms to move from high concentration regions to low concentration regions. The mechanism is typically by diffusion (molecular collisions).

4. **T** / **F** There are substances for which their experimentally measured entropy S(0) at T = 0 is not zero.

Answer: T See pages 94-95 of Schroeder, where the concept of residual entropy is discussed. This is an entropy associated with asymmetric objects like non-symmetric diatomic molecules such as CO (carbon monoxide), which you can think of as a tiny arrow that can stack in a crystal with its arrow pointing one way or the opposite way. It turns out that the disorder associated with irregular stacking is quite hard to remove (the relaxation time is extremely long) and so there is often a residual entropy even at absolute zero for some substances.

Note: I do expect you to read the assigned sections of Schroeder to learn about topics that I don't have time to discuss in lecture, of which residual entropy was an example.

5. **T** / **F** Consider an isolated system of two macroscopic subsystems A and B that each contain a mixture of two kinds of molecules, labeled type 1 and type 2, that can move between the two subsystems. If μ_{1A} denotes the chemical potential for molecule 1 in system A with a similar notation for other combinations of molecules and subsystems, then a necessary condition for the isolated system to be in thermodynamic equilibrium is: $\mu_{1A} = \mu_{1B} = \mu_{2A} = \mu_{2B}$.

Answer: F As discussed on pages 118-119 of Schroeder, each different constituent in some macroscopic system [say air which is a mixture of diatomic nitrogen (about 78% by volume), diatomic oxygen (about 21%), argon (about0.93%), and carbon dioxide (about 0.03%)] has its own chemical potential so thermodynamic equilibrium for a system holds only if the chemical potential for each component is the same in all parts of the system. But the chemical potentials themselves do not have to be the same. This is perhaps most clear from the qualitative observation that increasing the concentration of some substance increases its chemical potential. Thus for this problem in which there are two subsystems and two distinct molecules, you could imagine that the concentration of molecule 2 is small everywhere (corresponding to a large but constant chemical potential μ_1) while the concentration of molecule 2 is small everywhere (corresponding to a small but constant chemical potential μ_2). But there is no need for $\mu_1 = \mu_2$ throughout some substance and that would in fact be an unlikely occurrence (more than equilibrium would have to hold, one would have to tune some of the system parameters carefully).

Problems That Require Writing

1. (6 points) The Sun has a surface temperature of about 6000 K while the Earth has a surface temperature of about 300 K on a sunlit day. A square meter of Earth's surface receives about 1000 watts (J/s) of power from sunlight when the Sun is high in the sky. From this information and assuming eight hours of daylight per day, estimate to one significant digit the total change in entropy (Earth plus Sun) when a square meter of soil is exposed to sunlight for a 30-day month.

Note: You can compare your answer with the decrease in entropy associated with growing several kilograms of plants on this square meter of land over a month. In an earlier homework problem (2.36 of Schroeder), you learned to estimate the order-of-magnitude of the entropy associated with N particles, namely $S \approx Nk$. Several kilograms of plants corresponds to about 1,000 moles of atoms and so the entropy decrease associated with the plant growth should be of order $\Delta S \approx -Nk \approx -[1,000 \text{ moles} \times (6 \times 10^{23} \text{ atoms/mole})] \times (1.4 \times 10^{-23} \text{ J/K}) \approx -10^4 \text{ J/K}.$

Answer: $\Delta S_{\text{total}} \approx 3 \times 10^6 \, \text{J/s}.$

You first had to recognize that these are isothermal entropy processes, so the appropriate formula to use is $\Delta S = Q/T$ where Q is the heat that enters or leaves the system of interest while the temperature Tis assumed constant. (This formula is usually appropriate to use when the system receiving the heat or losing the heat is so large that there is no significant change in temperature, definitely the case for the Earth's surface and the Sun's surface.) For the more general case in which the temperature varies as heat is transferred, one would have to integrate, using Eq. (3.21) on page 94 or Eq. (3.50) on page 113 of Schroeder, in which you would have to know how the heat capacity C(T) varies with temperature over the range of interest.

The total entropy change is the increase in entropy at the Earth's surface with temperature T = 300 K (increase since the Earth is receiving heat) plus the decrease in entropy at the Sun's surface with

temperature $T = 6,000 = 20 \times 300$ (decrease since heat is leaving the Sun in the form of radiation). Thus

$$\Delta S_{\text{total}} = \Delta S_{\text{Earth}} + \Delta S_{\text{Sun}} \tag{1}$$

$$= \frac{Q}{T_{\text{Earth}}} - \frac{Q}{T_{\text{Sun}}}$$
(2)

$$=\frac{Q}{T_{\text{Earth}}}\left(1-\frac{T_{\text{Earth}}}{T_{\text{Sun}}}\right)$$
(3)

$$=\frac{19}{20}\frac{Q}{T_{\rm Earth}}\tag{4}$$

$$\approx \frac{Q}{T_{\text{Earth}}}.$$
 (5)

Here I used the observation that $T_{\text{Earth}}/T_{\text{Sun}} = \frac{1}{20}$ and $19/20 = 95/100 = 0.95 \approx 1$ to one digit. So it remains to estimate the entropy change on Earth to one digit:

$$\Delta S_{\text{Earth}} = \frac{Q}{T} \tag{6}$$

$$= \frac{1}{300 \,\mathrm{K}} \times \left[30 \,\mathrm{days} \times 8 \,\frac{\mathrm{hr}}{\mathrm{day}} \times 3600 \,\frac{\mathrm{s}}{\mathrm{hr}} \times 1000 \,\frac{\mathrm{J}}{\mathrm{s}} \right] \tag{7}$$

$$=\frac{3\times8\times3.6}{3}\times10^{1+3+3-2}$$
(8)

$$\approx (8 \times 4) \times 10^5 \,\mathrm{J/s} \tag{9}$$

$$\approx 3 \times 10^6 \,\mathrm{J/s.}$$
 (10)

where I rounded 3.6 to 4 and rounded 32 to 30. Several students were not careful and used 24 hours per day but there is, on average, only about 8 hours of sunshine per day in the lower latitudes.

- 2. (6 points) Consider an equilibrium paramagnet that consists of N magnetic dipoles each of magnitude μ . The paramagnet is at temperature T in the presence of a uniform magnetic field of strength B. For two points each, draw qualitatively
 - (a) the total magnetization $M/(N\mu)$ as a function of temperature $kT/(\mu B)$. (Note that $-1 \le M/(N\mu) \le 1$ and $-\infty \le kT/(\mu B) < \infty$.)
 - (b) the temperature $kT/(\mu B)$ as a function of energy $U/(\mu B)$. (Note that $-1 \le U/(\mu B) \le 1$.)
 - (c) The specific heat C/(Nk) as a function of temperature $kT/(\mu B)$.

For this problem only, you do *not* have to write anything to justify these figures.

Answer: See Figure (3.9) on page 101 and Figure (3.10) on page 103 of Schroeder for the answers. For the extremely few models that we discuss in full detail in this course—such as the ideal gas, Einstein solid, and paramagnet—I would like you to understand the physics of these systems, which means to have a qualitative understanding of how key properties of this system such as entropy, specific heat, and magnetization vary with temperature, energy, and magnetic field strength. It is not apparent from this course, since you are just learning thermal physics for the first time, but these simplified toy models, with a handful of others that you may come across later such as the Ising model of interacting magnetic spins, are a major source of intuition and understanding for much more complicated systems that are too hard to study from first principles. They are very much worth your time to think carefully about.

So you should take the time to think about the qualitative shapes of curves likes those in Fig. (3.10) and see if they make sense, either directly in terms of physical intuition, or in terms of what is being discussed in the text. As one example, all heat capacities C(T) must vanish in the limit $T \to 0$ (see page 95 of Schroeder) and yet quite a number of students drew heat capacity curves that were finite

at T = 0. Because the energy of a paramagnet is bounded, its heat capacity behaves differently than the heat capacity of an ideal gas or Einstein solid in that it increases and then decreases rapidly with increasing temperature.

If you understand conceptually that the magnetization of a paramagnet reflects a competition between the magnetic field strength B, which tries to align magnetic dipoles parallel to the field lines, and finite temperature, which tends to randomize the direction of a dipole through collisions, then you could guess without calculation that the largest possible magnetization of 1 (when measured on the "natural" scale of $N\mu$) corresponding to all dipoles aligned parallel to the magnetic field, can only occur at the lowest possible temperature T = 0, and M.

Even though the quiz gave you the formula for the magnetization as a function of temperature, Eq. (3.32) on page 104 of Schroeder, many students were not careful and did not notice that the formula has the form $\tanh(\mu B/kT)$ in which the temperature appears in the denominator of the argument. So they ended up plotting M vs 1/T which was not what was asked for.

One last comment. The specific heat C = dU/dT is obtained by differentiating the energy U of the system. You should be able to show, either qualitatively by drawing a picture or rigorously by using the definition of a derivative, that differentiation converts an even function f(x) = f(-x) into an odd derivative, f'(x) = -f'(-x) and vice versa (differentiation converts an odd function into an even derivative). The equation $U = -N\mu B \tanh(\mu B/kT)$ is an odd function with respect to T ($\tanh(x)$ is an odd function and so the substitution $T \to -T$ changes the sign of the energy) and so the specific heat dU/dT must be an even function of temperature. This elementary observation allows you to draw the specific heat of a paramagnet over the entire temperature range $-\infty < T < \infty$ as just the reflection of the specific heat curve for $T \ge 0$, which is shown in Fig. 3.10 on page 103. Schroeder shows just the non-negative range of T in his figure (which is reasonable, this is the part that is easiest to study experimentally).

3. (4 points) The entropy S = S(N, U, A) of an ideal two-dimensional monoatomic gas consisting of N atoms, energy U, and area A is given by the following version of the Sackur-Tetrode equation:

$$S = Nk \left[2 + \ln \left(\frac{2\pi m}{h^2} \frac{A}{N} \frac{U}{N} \right) \right].$$
(11)

Derive an expression for the pressure P of this two-dimensional gas, simplify your expression as much as possible, and discuss briefly whether your expression makes sense physically.

Answer:

$$P = \frac{NkT}{A}.$$
(12)

The only thinking required for this problem was to recognize that one had to use a different thermodynamic identity for a two-dimensional substance, of the form

$$dU = TdS - PdA + \mu dN,\tag{13}$$

where the work term -PdV had to be changed to an appropriate expression involving two-dimensional quantities, which would be an area A and something corresponding to "force per something" where the something must be per length instead of area to make the units work out. It is probably not a good idea to use the same symbol P to denote the usual pressure (force per area) and to denote the two-dimensional pressure (force per length), for example one could have problems in which a surface gas interacts with a volumetric gas¹.

¹You may want to read about the invention of the modern argon-filled light bulb by the physicist-chemist and later Nobel prize winner, Irving Langmuir. As a fresh PhD, he was hired by General Electric to break Edison's patents on the light bulb, but also to make a better light bulb, since Edison's carbon filament bulb burned out too quickly. Contrary to what everyone thought at the time, which was that one should create a better vacuum inside the bulb to reduce oxidation of the filament, Langmuir made several remarkable discoveries about how atoms from the filament were condensing on the inside of the bulb, and found that it was better to fill the bulb with an inert gas like argon to reduce the evaporation of the filament. The fields of surface chemistry and surface physics were basically started by Langmuir's careful and insightful attempts to improve the light bulb.

Once you had the appropriate thermodynamic identity, you could derive an expression for the twodimensional pressure by assuming dU = 0 and dN = 0 in which case:

$$P = T \left. \frac{\partial S}{\partial A} \right|_{U,N},\tag{14}$$

which is the analogy of the formula $P = T\partial S/\partial V$ that we have used for 3d gases. It is straightforward to differentiate the 2d Sackur-Tetrode with respect to A and obtain Eq. (12). This has exactly the same form as the ideal gas equation PV = NkT (also called Clapeyron's equation since the French scientist Clapeyron was the first to write down the full ideal gas law way back in the early 1800s), and so is reasonable for the same reason that the ideal law is reasonable. For example, for a fixed area A and for a fixed number of particles N, raising the temperature T increases the pressure P, and so on.

I challenge you to think about how to verify Eq. (12) experimentally. For example, how would you measure or vary the pressure, area, and number of particles for a two-dimensional gas adsorbed on the surface of some substrate? Is it possible to carry out isothermal and adiabatic compressions of a two-dimensional gas? Can you carry out some thermodynamic cycle like those shown in Fig. 1.10 on page 23 (except on a P - A plane) and so create little two-dimensional heat engines or refrigerators? You might enjoy browsing the images on IBM's scanning tunneling microscope (STM) website

http://www.almaden.ibm.com/vis/stm/gallery.html

which shows that scientests for many years now have had the ability to manipulate single atoms on surfaces, e.g. write the word "IBM" with xenon atoms on a nickel surface. So it is possible to build little walls to contain a two-dimensional gas and those walls will feel a pressure from the gas trapped inside of them.