Quiz 3 for Physics 176: Answers

Professor Greenside

True or False Questions (2 points each)

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

1. **T / F** If the volume V of an ideal monoatomic gas is halved during an isothermal compression that conserves the number of particles, then the entropy of the gas will decrease by $Nk\ln(2)$.

   Answer: T This was discussed in Schroeder and in lecture and is a direct consequence of the Sackur-Tetrode equation, which was given on the first page of the quiz. If the number of particles N and total particle energy U are fixed, then Sackur-Tetrode says that $S = Nk\ln(V) + f(N, U)$, where f is a function that depends only on N and U and so does not change during a volume change and so can be ignored when computing the entropy change. This problem needed to assume an isothermal compression to prevent the energy U from changing during the compression.

   Thus the change in entropy during the isothermal compression of an ideal monoatomic gas is $\Delta S = S_f - S_i = Nk\ln(V_f) - Nk\ln(V_i) = Nk\ln(V_f/V_i)$. For this problem, $V_f/V_i = 1/2$ so the change in entropy is $\Delta S = Nk\ln(1/2) = -Nk\ln(2)$, which is indeed a decrease in the entropy by the magnitude $Nk\ln(2) \approx 0.7Nk$.

2. **T / F** The product of an extensive thermodynamic quantity with an intensive thermodynamic quantity is also an extensive quantity.

   Answer: T This question was intended to test whether you understood my brief description in class about extensive variables like M, V, S, and U versus intensive variables like P, T, $\rho = M/V$, $n = N/V$, and so on. Extensive variables increase in proportion to the volume of the system (keeping the density N/V constant), e.g. if you double the volume you typically double the entropy and the mass. Intensive variables are almost always ratios of two extensive variables and so don't change when the volume is varied. From this, you should be able to see that the product of an extensive variable with an intensive variable remains extensive: changing the volume causes the extensive variable to change, but the intensive factor does not change.

3. **T / F** Given that the function $f(x) = 1 - x^4$ has a single maximum at $x_{\rm max} = 0$ with value $f_{\rm max} = 1$, the function $[f(x)]^N$ for N a large integer can be accurately approximated by a Gaussian e^{-NAx^2} for $A > 0$ some constant.

   Answer: F This question was intended to see if you could think rather than just memorize. In class, we discussed a "theorem", that a function $f(x)$ with a unique global maximum, if raised to a large power N, $f(x)^N$, behaves like a narrow Gaussian function centered on the location $x_{\rm max}$ of the global maximum. The derivation involved taking the log of the function $f(x)^N$ to get $N\log(f(x))$, Taylor expanding $f(x)$ about $x = x_{\rm max}$, and using our favorite log approximation $\log(a+\epsilon) \approx \log(a) + \epsilon/a$.

   A key step in the derivation was taking the Taylor expansion to second order:

$$
\begin{aligned}
f(x) &= f\left(x_{\rm max}\right) + f'\left(x_{\rm max}\right)\left(x - x_{\rm max}\right) + \frac{1}{2!} f''\left(x_{\rm max}\right)\left(x - x_{\rm max}\right)^2 + \ldots \qquad (1) \\
&\approx f_{\rm max} + \frac{f''\left(x_{\rm max}\right)}{2}\left(x - x_{\rm max}\right)^2 . \qquad (2)
\end{aligned}
$$

   But this procedure only works if the Taylor expansion has a nonzero coefficient $f''(x_{\rm max})$ at the location of the global maximum, otherwise you get some other kind of functional behavior that is not a Gaussian.

Indeed, if we write $F_N(x) = (1 - x^4)^N$, then

$$\log(F_N) = N \ln\left(1 - x^4\right) \approx -N x^4, \tag{3}$$

since sufficiently near the global maximum $x = 0$, $|x| \ll 1$, so $x^4 \ll 1$ and so $\ln(1 - x^4) \approx -x^4$. Exponentiating both sides gives us:

$$F_N = \left(1 - x^4\right)^N \approx \exp\left(-N x^4\right), \tag{4}$$

which is not a Gaussian, but some function that decays more rapidly than a Gaussian as $|x| \to \infty$.

4. **T / F** For any sequence of experimental steps that leads to a change ΔS_{gas} in the entropy of an ideal monoatomic gas (because the variables N, V, and U of the gas have changed to new values N', V', and U'), the value ΔS_{gas} will depend on how the variables N, V, and U were changed to their new values (e.g., quasistatic or not quasistatic, isothermal versus adiabatic, etc.)

   Answer: F The entropy S of a system, like the energy U of a system, is a function of system properties such as N, V, and U and so depends only on the current values of those numbers, not on the experimental history of how those properties were attained. This is apparent for example from the Sackur-Tetrode equation for a monoatomic ideal gas, the formula $S = S(N, V, U)$ does not require knowledge of how the system was prepared, just the current values of N, V, and U. Similarly, the formula for the multiplicity Ω of an Einstein solid depends only on the number N of oscillators and number of energy units q but not on how the solid was brought to its current state, and similarly for a paramagnet consisting of N magnetic dipoles.

   In thermodynamics, properties of a system that depend only on the current values of system parameters are called "state variables" since they depend only on the current macroscopic state of the system. Schroeder does not mention this concept but most other books on thermal physics do.

5. **T / F** For any sequence of experimental steps that leads to a change in the entropy of an ideal monoatomic gas (because the variables N, V, and U of the gas have changed to new values N', V', and U'), the total change in entropy of the gas and surrounding environment will depend on how the variables N, V, and U were changed to their new values

   Answer: T The answer here is true because of the difference between reversible and irreversible processes. Any sequence of processes applied to an ideal gas (or some other thermodynamic system) will cause its entropy to change to a value that depends on the final value of the system parameters N, V, and U. But the total entropy generated—gas plus surrounding environment—will depend on whether reversible or irreversible processes were used during the sequence, e.g., a non-quasistatic compression that is so rapid that the gas is not in thermal equilibrium during the compression.

6. **T / F** The process of slowly, quasistatically, and isothermally introducing a thin impermeable partition into a box of an ideal gas such that the partition divides the volume V of the box in two volumes of $V/3$ and $2V/3$ is an example of a reversible thermodynamic process.

   Answer: T This is an important point made by Schroeder on the first paragraph of page 80: mixing of gases consisting of the same particles, e.g., by introducing a partition that reduces the volume available to different parts of a gas, does not change the entropy of the system. In fact, it was to achieve this goal that Gibbs introduced the somewhat mysterious $1/N!$ factor in the expression Eq. (2.38) for the multiplicity of an ideal gas of N identical particles in a volume V, otherwise introducing a withdrawing a partition would cause an entropy change.

Multiple Choice Questions (4 points each)

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

1. If x is a sufficiently small number, then the lowest-order approximation to the expression

$$\ln(1-x)+\ln(1+x)+\ln(1+x^2)+\ln(1+x^4),$$

is

(a) x^2 (b) $-x^2$ (c) x^4 (d) $-x^4$ (e) x^6 (f) $-x^8$.

Answer: (f) Solving this question required you to understand why many of you got the wrong answer in Problem 2.24(b) on page 67 of Schroeder. As I discussed at the beginning of one of the lectures, there was a point in the algebra of 2.24(b) where many of you faced an expression of the form

$$\frac{N}{2}\ln\left(\frac{N}{2}-x\right)+\frac{N}{2}\ln\left(\frac{N}{2}+x\right), \tag{5}$$

which many of you simplified to be approximately $N\ln(N/2)$, independent of x, since $\ln(N/2-x)\approx\ln(N/2)-2x/N$ and $\ln(N/2+x)\approx\ln(N/2)+2x/N$ for $|x|\ll 1$, so the terms containing an x cancel. But this just says that the lowest power in x vanishes, there could be higher-powers to consider and indeed one has[1]:

$$\begin{aligned}
&\frac{N}{2}\ln\left(\frac{N}{2}-x\right)+\frac{N}{2}\ln\left(\frac{N}{2}+x\right) && (6)\\
&\quad=\frac{N}{2}\ln\left[\left(\frac{N}{2}-x\right)\left(\frac{N}{2}+x\right)\right] && (7)\\
&\quad=\frac{N}{2}\ln\left[\left(\frac{N}{2}\right)^2-x^2\right] && (8)\\
&\quad=\frac{N}{2}\ln\left[\left(\frac{N}{2}\right)^2\times\left(1-\frac{x^2}{(N/2)^2}\right)\right] && (9)\\
&\quad=\frac{N}{2}\ln\left[\left(\frac{N}{2}\right)^2\right]+\frac{N}{2}\ln\left[1-\left(\frac{2x}{N}\right)^2\right] && (10)\\
&\quad\approx N\ln\left(\frac{N}{2}\right)-\frac{2}{N}x^2, && (11)
\end{aligned}$$

to second-order in the small quantity x^2. This nonzero second-order piece then combined with other second-order pieces to give a Gaussian $\exp(-2x^2/N)$ while most of you derived the approximation $\exp(-4x^2/N)$.

With this insight in mind, you should now be able to see that

$$\begin{aligned}
&\ln(1-x)+\ln(1+x)+\ln\left(1+x^2\right)+\ln\left(1+x^4\right) && (12)\\
&\quad=\ln\left[(1+x)(1-x)\right]+\ln\left(1+x^2\right)+\ln\left(1+x^4\right) && (13)\\
&\quad=\ln\left(1-x^2\right)+\ln\left(1+x^2\right)+\ln\left(1+x^4\right) && (14)\\
&\quad=\ln\left(1-x^4\right)+\ln\left(1+x^4\right) && (15)\\
&\quad=\ln\left(1-x^8\right) && (16)\\
&\quad\approx -x^8, && (17)
\end{aligned}$$

so the answer is (f).

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[1] You can get the same result but with slightly more effort by using the second-order approximation

$$\ln(a+\epsilon)\approx\ln(a)+\frac{x}{a}-\frac{1}{2}\left(\frac{x}{a}\right)^2+\ldots$$

.

Problems That Require Writing

All answers in this section of the quiz must be written on the supplementary blank pages. Please remember to write your name and problem number on each extra page.

1. (5 points) The multiplicity Ω of a certain substance is related to its thermal energy U by the relation $\Omega = aU^b$, where a and b are positive constants. Find a formula for the heat capacity C_V of the substance in terms of a, b, and the Boltzmann constant k.

   Answer: $C_v = kb$.

   This problem involved straightforward algebra, using basic definitions. From the multiplicity Ω, we get the entropy $S = k\ln\Omega$, which then gives the temperature $1/T = \partial S/\partial U$ which can be solved for $U = U(T)$ which then gives the specific heat $C_V = dU/dT$. The corresponding algebra is

   $$S = k\ln\Omega = k\ln\left(aU^b\right) \qquad \Rightarrow \qquad \frac{1}{T} = \frac{dS}{dU} = \frac{d}{dU}\left[k(\ln(a) + b\ln U)\right] = \frac{kb}{U}, \tag{18}$$

   so $U = kbT$ and $C_V = dU/dT = kb$.

   Several students in the class wrote:

   $$\ln(aU^b) = b\ln(aU), \tag{19}$$

   a math error of a sort that should not happen for students taking a sophomore-level or higher physics course.

2. (15 points) Many scientists and engineers are greatly interested in the properties of molecules that adsorb onto the surface of a substance. ("Adsorb" means that a molecule leaves the gas phase and bonds with the surface.) For sufficiently high temperatures and for some weakly binding surfaces (e.g. graphite or frozen argon), the adsorbed molecules can move freely about on the surface without interacting with each other and so act like a two-dimensional ideal gas.

   Consider N identical atoms, each of mass m, that have adsorbed onto a flat surface of area A and of temperature T. **Derive an appropriate version of the Sackur-Tetrode equation that describes the entropy $S = S(N, A, U)$ of a two-dimensional ideal gas of monoatomic atoms as a function of N, A, and the thermal energy U.**

   Some comments: By analogy to how we derived the multiplicity Ω of an ideal gas in a three-dimensional volume, first derive an expression for the multiplicity Ω of the two-dimensional ideal gas. Each adsorbed molecule is free to move about in a two-dimensional area A, and each adsorbed molecule is described by a two-dimensional momentum vector $\mathbf{p} = (p_x, p_y)$ with kinetic energy $p^2/(2m) = (p_x^2 + p_y^2)/(2m)$. For this problem, assume that the N adsorbed atoms are an isolated system so that their total energy is conserved. After you have obtained an expression for the multiplicity, use the definition of entropy plus Stirling's approximation to derive the 2D version of the Sackur-Tetrode equation. You can drop multiplicative factors of a very large number that are small or large numbers.

   Answer:

   $$S = Nk\left[2 + \ln\left(\frac{2\pi m}{h^2}\,\frac{A}{N}\,\frac{U}{N}\right)\right]. \tag{20}$$

   This was another problem where I was interested whether you understood the assumptions and details of how the multiplicity Ω of an ideal gas was determined. The details *are* worth understanding since ideal gases play such an important role in physics and chemistry, and an ideal gas is one of the few systems for which all the details can be worked out analytically. (Three other solvable systems that we discuss in the course are the Einstein solid, paramagnet, and rubber band.)

Each adsorbed molecule can glide around on the surface in an area A and the essence of the particles being in an ideal gas is that they move about independently, with the motion of one molecule not affecting the motion of another molecule. So we deduce $\Omega \propto A^N$, just as for the 3D gas we had $\Omega \propto V^N$.

Since the particles move around on a two-dimensional surface, each particle is characterized by a two-dimensional momentum vector $\mathbf{p} = (p_x, p_y)$ and so the total energy U of this isolated system is given by the sum of the kinetic energies $p^2/(2m)$ of each particle:

$$U = \frac{\mathbf{p}_1^2}{2m} + \ldots + \frac{\mathbf{p}_N^2}{2m} \tag{21}$$

$$= \frac{1}{2m}\left(p_{1x}^2 + p_{1y}^2 \; + \; p_{2x}^2 + p_{2y}^2 \; + \; \ldots \; + \; p_{Nx}^2 + p_{Ny}^2\right). \tag{22}$$

which can be written in the form

$$p_{1x}^2 + p_{1y}^2 \; + \; p_{2x}^2 + p_{2y}^2 \; + \; \ldots \; + \; p_{Nx}^2 + p_{Ny}^2 = \left(\sqrt{2mU}\right)^2, \tag{23}$$

which is the equation for a $2N$-dimensional hypersphere of radius $\sqrt{2mU}$. (For the 3d gas, we had a $3N$-dimensional sphere since the momentum vector for each of the N particles contributed three numbers.) Thus we expect $\Omega \propto A_{2N}(\sqrt{2mU})$ where $A_d(r)$ is the surface area of a d-dimensional sphere of radius r.

Putting the above together, we finally get the following expression for the multiplicity of a 2d ideal gas:

$$\Omega = \frac{1}{N!}\frac{A^N A_{2N}(\sqrt{2mU})}{(h^2)^N}. \tag{24}$$

The factor $1/N!$ is required since we have assumed the particles to be identical. The factor $1/h^{2N}$ involving Planck's constant is required to count the number of states; we need one factor of h for the product $L_x \times p_x$ of length times momentum and another factor h for the product $L_y \times p_y$ (where we can think of $A = L_x L_y$) and we have to raise h^2 to the Nth power to take into account N distinct products of areas with momentum areas, $L_x L_y \times p_x p_y$.

Once we have Eq. (24) for the multiplicity, we can substitute the given expression for the surface area of a $d = 2N$-dimensional sphere of radius $r = \sqrt{2mU}$, and simplify using Stirling's formula. We have

$$\Omega = \frac{A^N}{N!\, h^{2N}} \times \frac{2\,\pi^{(2N)/2}}{\Gamma\left(\frac{(2N)}{2}\right)}\left(\sqrt{2mU}\right)^{(2N)-1}. \tag{25}$$

Since we are assuming N is a large number, we can drop the 2 multiplying the π^N as being a small number multiplying a big number π^N, and we can approximate $2N - 1 \approx 2N$ when raising the radius $\sqrt{2mU}$ of the momentum sphere to $2N - 1$. We also can approximate the Gamma function in the denominator by

$$\Gamma(N) = (N-1)! \approx N!\,. \tag{26}$$

With these approximations, the multiplicity becomes

$$\Omega = \frac{A^N \pi^N}{(N!)^2\, h^{2N}}(2mU)^N = \frac{1}{(N!)^2}\left(\frac{2\pi m A U}{h^2}\right)^N. \tag{27}$$

Stirling's formula gives

$$(N!)^2 \approx \left(\sqrt{2\pi N}\left(\frac{N}{e}\right)^N\right)^2 \approx 2\pi N\left(\frac{N}{e}\right)^{2N} \approx \left(\frac{N}{e}\right)^{2N}, \tag{28}$$

where we can drop the $2\pi N$ prefactor as a large number multiplying a very large number $(N/e)^{2N}$. Combining Eq. (28) with Eq. (27) gives

$$\Omega = \left(\frac{2\pi e^2 m}{h^2}\frac{A}{N}\frac{U}{N}\right)^N, \tag{29}$$

where I have written the expression in terms of the intensive parameters A/N and U/N. We can then finish by taking the log to get the entropy:

$$S = k \ln \Omega = Nk \ln \left(\frac{2\pi e^2 m}{h^2} \frac{A}{N} \frac{U}{N} \right) = Nk \left[2 + \ln \left(\frac{2\pi m}{h^2} \frac{A}{N} \frac{U}{N} \right) \right]. \tag{30}$$

It is perhaps worth splitting off the 2 (from the e^2) to emphasize that the entropy will be of order Nk in magnitude.