Quiz 3 Answers
February, 2011

1. To two significant digits,

$$k \simeq 1.4 \cdot 10^{-23} \frac{J}{K}$$

Please memorize this value over the semester, I do not plan to provide it in future exams or quizzes.

The units can be deduced in several ways, easiest is to use equipartition for an atomic ideal gas:

$$\underbrace{\left\langle \frac{1}{2} m v^2 \right\rangle}_{\text{units of energy or joule}} = \frac{3}{2} k \underset{\uparrow}{T}$$

units of kelvin

Crucial that T be an absolute temperature for this expression to make sense, T=0 is absolute zero.

2a For an Einstein solid with N identical oscillators and q units of energy, if $N \gg q \gg 1$, this means that the number of energy units per oscillator q/N <u>on average</u> will be a small number

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so most oscillators will be in their lowest energy state, or ground state. But the lowest possible energy is $q=0$, all oscillators in their ground state, and this must correspond to absolute zero $T=0$.

So $N \gg q \gg 1$ implies the Einstein solid must be close to absolute zero, a low-temperature regime.

2b.) The discussion is <u>exactly</u> similar to pages 63-64 of Schroeder and to what I discussed in lectures; as long as you sweated these details, you should have been able to answer this question.

In fact, if you remembered or ~~know~~ knew that the high temperature limit $q \gg N \gg 1$ led to the approximation

$$\Omega = \binom{q+N-1}{q} \simeq \frac{(q+N)!}{q!\,N!} \simeq \left(\frac{eq}{N}\right)^N$$

and realized that $\Omega \simeq \frac{(q+N)!}{q!\,N!}$ is symmetric with respect to the symbols q and N, you would have

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realized that the answer to 2b was obtained by simply swapping the symbols q and N

$$\left(\frac{eq}{N}\right)^N \xrightarrow[N\to q]{q\to N} \left(\frac{eN}{q}\right)^q \quad \text{for } q \gg N \gg 1$$

But I did want you to show me that you mastered the key techical details:

1. take $\ln \Omega$ to simplify the math
2. use Stirling to simplify the factorials $\ln(n!) \simeq n\ln n - n$
3. Look for terms of form $\ln(N+q) \simeq \ln N + q/N$ since $q/N \ll 1$

Too many students avoided using a log and ended up with expressions like

$$\Omega(N,q) \simeq \frac{\sqrt{2\pi(N+q)}\left(\frac{N+q}{e}\right)^{N+q}}{\sqrt{2\pi q}\left(\frac{q}{e}\right)^q \sqrt{2\pi N}\left(\frac{N}{e}\right)^N} \simeq \left(\frac{N+q}{q}\right)^q \left(\frac{N+q}{N}\right)^N$$

and then said: "oh, $N \gg q$ so let's replace $N+q \simeq N$"

which would give

$$\Omega(N,q) \simeq \left(\frac{N}{q}\right)^q$$

but then where does the e^q term come from? Key point is that one has to retain small quantities of order q/N by a perturbation or series approximation, and this leads to the e^q factor.

If you remember your intro calculus, that

$$\lim_{N\to\infty} \left(1+\frac{q}{N}\right)^N \simeq e^q, \qquad (*)$$

you could have gotten the answer without using $\ln \Omega$, but you derive $(*)$ by taking log's:

$$y = (1+q/N)^N$$

$$\ln y = N \ln\left(1+\frac{q}{N}\right) \simeq N\left(\frac{q}{N}\right) \simeq q \quad \text{if } q \ll N$$

$$\Rightarrow \quad y \simeq e^q \text{ for big } N$$

Best bet: take log of an expression when dealing with a very large number

(2C) Starting with $\Omega(N;q) \simeq \left(\frac{eN}{q}\right)^q$ and using $U = \epsilon q$, we would proceed as follows to get the heat capacity $C = \frac{dU}{dT}$:

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$$S = k\ln\Omega = k\ln\left[\left(\frac{eN}{q}\right)^q\right]$$

$$= kq\left[\ln(Ne) - \ln(q)\right]$$

Now get temperature from $\frac{1}{T} = \frac{\partial S}{\partial U}$:

$$\frac{1}{kT} = \frac{\partial \ln\Omega}{\partial U} = \frac{\partial\ln\Omega}{\partial q}\frac{\partial q}{\partial U} = \frac{1}{\epsilon}\frac{\partial\ln\Omega}{\partial q}$$

$$= \frac{1}{\epsilon}\frac{\partial}{\partial q}\left[q\left(\ln(Ne) - \ln(q)\right)\right]$$

$$= \frac{1}{\epsilon}\left[\ln(Ne) - \ln(q) + q\left(-\frac{1}{q}\right)\right]$$

$$= \frac{1}{\epsilon}\left[\ln N + \underbrace{\ln e}_{=1} - \ln q - 1\right]$$

$$\boxed{\frac{1}{kT} = \frac{1}{\epsilon}\left[\ln N - \ln q\right] = \frac{1}{\epsilon}\ln\left[\frac{N}{q}\right] = \frac{1}{\epsilon}\ln\left[\frac{N\epsilon}{U}\right]}$$

This can be rewritten to solve for $U = U(T)$:

$$\frac{\epsilon}{kT} = \ln\left(\frac{N\epsilon}{U}\right) \Rightarrow e^{\epsilon/kT} = \frac{N\epsilon}{U}$$

or $\boxed{U = (N\epsilon)\,e^{-\epsilon/kT}}$

Note details of this expression that make sense: left side is energy, right side has units $N\epsilon$ of energy and argument of exponential $\frac{\epsilon}{kT}$ must be dimensionless, which it is since ϵ has units of energy as does kT.

Final step is just to differentiate to get C:

$$C = \frac{dU}{dT} = N\epsilon \frac{d}{dT}\left(e^{-\epsilon/kT}\right) = N\epsilon\left[e^{-\epsilon/kT} \times \underbrace{\frac{d}{dT}\left(-\frac{\epsilon}{kT}\right)}_{\text{by chain rule}}\right]$$

$$\boxed{C = Nk \cdot \left(\frac{\epsilon}{kT}\right)^2 e^{-\epsilon/kT}} \qquad (*)$$

which was the desired answer. This agrees with what you did in a recent homework problem and agrees with the low-T limit of the full expression

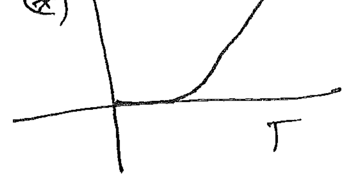
$$C = Nk\left(\frac{\epsilon}{kT}\right)^2 \frac{e^{\epsilon/kT}}{\left(e^{\epsilon/kT}-1\right)^2},$$

for an Einstein solid, valid for all values of T.

You should be able to verify, say by <u>L'Hôpital's rule</u>, that

$$\lim_{T\to 0} \left(\frac{\epsilon}{kT}\right)^2 e^{-\epsilon/kT} = 0$$

(*)



Quiz 3 solutions

Multiple choice 1 : answer is (d), $(A_3(R))^N A_{2N}(\sqrt{2mU})$

Reason is following: if gas is ideal, molecules don't interact with one another so multiplicity will be proportional to "space available to particle 1" × "space available to particle 2" × ... × "space available to particle N"

But if particles move on sphere of radius R, the available space is the surface area $A_3(R)$. So we conclude

$$\Omega \propto [A_3(R)]^N \quad \text{if gas is ideal}$$

which rules out answers (a), (c), and (e).

Next important insight is that particles are moving on surface of sphere, which is a two-dimensional domain. So momentum vector (p_x, p_y, p_z) of given particle, although a 3-vector, is constrained to be tangent to the sphere, so there are only two independent components. We conclude

$$\Omega \propto [A_3(R)]^N A_{2N}(\sqrt{2mU})$$

because surface of sphere is 2D, reduced dimensionality

Quiz 3 Solution

True False

1. T/F is False, see middle of page 57 of Schroeder

2. False This was key point of discussion on pages 57-59 of Schroeder. In an isolated Einstein solid consisting of two subsystems A and B, if A has energy q_A and B has energy q_B, then over short times (compared to a thermal relaxation time L^2/K), the multiplicity of the entire system is given approximately by

$$\Omega_{total} \simeq \Omega_A(q_A)\,\Omega_B(q-q_A)$$

But over longer times, when equilibrium is attained, the total multiplicity can be much bigger

$$\Omega_{total} = \binom{N_A+N_B+q_A+q_B-1}{q_A+q_B}$$

The total multiplicity can and does change with time (unless one started already in equilibrium) and increases steadily until the multiplicity reaches a maximum. This is in fact the second law of thermodynamics, $\frac{dS}{dt} \geq 0$, expressed in terms of the multiplicity Ω.

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True-false

3. false The Sackur-Tetrode equation given in the quiz,

$$S = Nk\left[\frac{5}{2} + \ln\left(\frac{V}{N}\left(\frac{4\pi m}{3h^2}\frac{U}{N}\right)^{3/2}\right)\right]$$

depends on the mass of the atoms in the gas. In fact:

$$S = \frac{3}{2}Nk\ln(m) + \text{other stuff not dependent on } m$$

So increasing the atomic mass m directly increases the entropy since $\ln(x)$ is a monotone increasing function of x. Argon has a greater entropy than He.

4. True This was a point made in lecture and you were asked in a homework problem, Problem 2.7 of Assignment 5, to show directly that you could apply Einstein's theory of a solid to the vibrational modes of a diatomic gas. In fact, Einstein's theory is more correctly applicable to the diatomic molecules than to crystalline vibrations since the molecules are exactly identical, while oscillators in a solid have a continuous range of frequencies and so are neither identical nor independent.

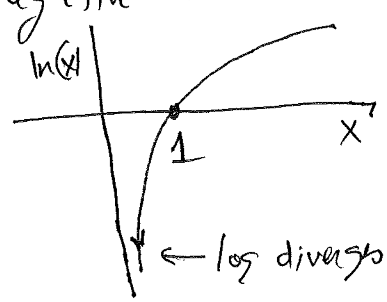
Quiz 3 answers

True-False

5. false By expanding the log in the Sackur-Tetrode equation given in the quiz, you can isolate the contributions of the variables U, V, and N.

$$S = Nk\ln V + \frac{3}{2}Nk\ln U - \frac{5}{2}N\ln N + \text{stuff}$$

where "stuff" doesn't depend on V, U, or N. From this form, we see immediately that making V sufficiently small and positive or making U sufficiently small and negative can make S negative since $\ln(x) \to -\infty$ as $x \to 0$:



This is unphysical: since $\Omega \geq 1$, $k\ln\Omega = S \geq 0$. The more physical criterion for Sackur-Tetrode giving a negative value comes from writing

$$S = Nk\left[\frac{5}{2} + \ln\left(\frac{V/N}{\lambda_D^3}\right)\right] \qquad \lambda = \frac{h}{\sqrt{2\pi mkT}}$$

If T (hence U) is small enough or V/N is small enough, $V/N \ll \lambda_D^3$ and S becomes negative.

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True-false

6. $(-1)! = \infty$ I graded this as true but the answer is strictly false, so please get in touch with me if you got this T/F marked wrong, so I can restore 2 points to your score.

First, I didn't expect you to have to do any calculation here, I was hoping that, as you read Schroeder's Appendix B.2 about the Gamma function, you had looked at the plot of $\Gamma(x)$ vs x in Fig. B.3 on page 388 and noticed that

$$|(-n)!| = \infty$$

for every positive integer $n \geq 1$, i.e., negative integer factorials have infinite magnitude. (I had left out the absolute value sign for the quiz, so $(-1)! = \infty$ or $-\infty$ are acceptable answers.) The actual value of $(-n)!$ for n a positive integer depends though from what side you take the limit $x \to -n$, from the left or right.

TF 6 continued

To understand what is going on, we can look at the formal value of x! for x any negative real number

$$x! = \Gamma(x+1) = \int_0^\infty t^x e^{-t}\,dt = \int_\epsilon^\infty t^x e^{-t}\,dt + \int_0^\epsilon t^x e^{-t}\,dt \qquad x<0$$

Here I have done a common trick for an integral that has a divergent integrand $t^x e^{-t} = \frac{e^{-t}}{t^{-x}} \to \infty$ as $t \to 0$ if $x<0$, I split the integral into a part close to the point of divergence, $\int_0^\epsilon$, when $\epsilon \ll 1$ is a tiny number, and a part $\int_\epsilon^\infty$ that is finite. For sufficiently small ϵ, $e^{-t} \simeq 1-t \simeq 1$ since t lies between $[0,\epsilon]$,

So $$\int_0^\epsilon t^x e^{-t}\,dt \simeq \int_0^\epsilon t^x\,dt = \left.\frac{t^{x+1}}{x+1}\right|_0^\epsilon = \frac{\epsilon^{x+1}}{x+1} - \lim_{\epsilon\to 0}\frac{t^{x+1}}{x+1}$$

For $x<-1$, this diverges to $-\infty$; for $x=-1$, the integral becomes $\int_0^\epsilon t^{-1}e^{-t}\,dt \simeq \int_0^\epsilon \frac{dt}{t} \simeq \ln\epsilon - \lim_{\epsilon\to 0}\ln\epsilon \to -\infty$, while for $-1<x<0$, the integral is finite.

So strictly speaking, x! diverges to $-\infty$ for $x \leq -1$ based on the integral. But mathematicians long ago observed that, while the integral diverged, one could get a finite value of x! for any x not a negative integer by using the recursion relation

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TF
6 cont'd:

$$\Gamma(x) = \frac{1}{x}\Gamma(x+1)$$

repeatedly until one was evaluating Γ at positive values. For example

$$\Gamma(-\sqrt{2}) \cong \Gamma(-1.4) = \frac{1}{(-\sqrt{2})}\Gamma(1-\sqrt{2})$$

$$= \frac{1}{(-\sqrt{2})}\frac{1}{(1-\sqrt{2})}\underbrace{\Gamma(2-\sqrt{2})}_{\text{finite positive value since } 2-\sqrt{2}>0}$$

For x negative and non-integer, let m be the integer closest to but larger than x, ~~x~~ $x < m < 0$. Then

$$\Gamma(x) = \frac{1}{x}\Gamma(1+x) = \frac{1}{x(1+x)}\Gamma(2+x) = \cdots = \frac{1}{x(1+x)\cdots(m+x)}\Gamma(m+1+x)$$

Again we end up with a finite value since x is not an integer and $\Gamma(m+1+x)$ is evaluated at a positive value. But now you can see why $x!$ diverges to $\pm\infty$ for x a negative integer, we can take the limit $x \to -k^+$ or $x \to -k^-$ and the factor $\frac{1}{x+k}$ will diverge to $\pm\infty$. So even with a definition in terms of the recursion relation, one can not avoid $(-n)!$ diverging for $n \geq 1$.