Problem 1

Kittel & Kroemer, Chapter 3, problem 6 [Rotation of diatomic molecules]

In our first look at the ideal gas we considered only the translational energy of the particles. But molecules can rotate, with kinetic energy. The rotational motion is quantized; and the energy levels of a diatomic molecule are of the form

$$\epsilon(j) = j(j+1)\epsilon_0$$

where j is any positive integer including zero: $j = 0, 1, 2, \ldots$. The multiplicity of each rotational level is $g(j) = 2j + 1$.

(a): 1 point

Find the partition function $Z_R(\tau)$ for the rotational states of one molecule. Remember that Z is a sum over all states, not over all levels—this makes a difference.

Let's see:

$$Z_R(\tau) = \sum_s e^{-j(j+1)\epsilon_0/\tau},$$

where the sum over all possible states. Each term in the partition function sum with energy $j(j+1)\epsilon_0$ will show up exactly $2j+1$ times. So we can write this sum as   (a): 1 point

$$Z_R(\tau) = \sum_{j=0}^{\infty} (2j+1)e^{-j(j+1)\epsilon_0/\tau}.$$

(b): 1 point

Evaluate $Z_R(\tau)$ approximately for $\tau \gg \epsilon_0$, by converting the sum to an integral.

This will be a one-dimensional integral: $\sum_{j=0}^{\infty} \to \int_0^{\infty} dj$. This is a good approximation when τ is large compared to the spacing between energy levels, which is $\approx \epsilon_0$. Thus in that regime,

$$Z_R(\tau) \approx \int_0^{\infty} (2j+1)e^{-j(j+1)\epsilon_0/\tau}dj.$$

Defining $x \equiv j(j+1)\epsilon_0/\tau$, $dx = (2j+1)(\epsilon_0/\tau)dj$, this becomes   (b): 1 point

$$Z_R(\tau) \approx \frac{\tau}{\epsilon_0}\int_0^{\infty} e^{-x}dx$$
$$= \frac{\tau}{\epsilon_0}.$$

(c): 1 point

Do the same for $\tau \ll \epsilon_0$, by truncating the sum after the second term.

At low temperatures, the first few terms in the sum dominate. Let's keep the first two, $j = 0$ and $j = 1$:   (c): 1 point

$$Z_R(\tau) \approx 1 + 3e^{-2\epsilon_0/\tau}.$$

(d): 1 point

Give expressions for the energy U and the heat capacity C, as functions of τ, in both limits. Observe that the rotational contribution to the heat capacity of a diatomic molecule approaches 1 (or, in conventional units, k_B) when $\tau \gg \epsilon_0$.

Let's start with the high-temperature limit $\tau \gg \epsilon_0$. In that case $Z_R(\tau) \approx \frac{\tau}{\epsilon_0}$, and so

$$U = \tau^2 \frac{\partial \ln Z}{\partial \tau} \approx \tau^2 \frac{\partial}{\partial \tau} \ln(\tau/\epsilon_0)$$
$$= \tau,$$

and

$$C_V = (\partial U/\partial \tau)_V = 1.$$

This makes sense from the point of view of the equipartition theorem: a diatomic molecule has 2 rotational degrees of freedom, each getting an average energy of $\frac{1}{2}\tau = \frac{1}{2}k_B T$ at high temperatures.

Now consider the opposite limit, $\tau \ll \epsilon_0$, for which $Z \approx 1 + 3e^{-2\epsilon_0/\tau} = 1 + 3e^{-2\beta\epsilon_0}$

$$U = -\frac{\partial \ln Z}{\partial \beta} \approx -\frac{\partial}{\partial \beta} \ln(1 + 3e^{-2\beta\epsilon_0})$$
$$= -\frac{-6\epsilon_0 e^{-2\beta\epsilon_0}}{1 + 3e^{-2\beta\epsilon_0}}$$
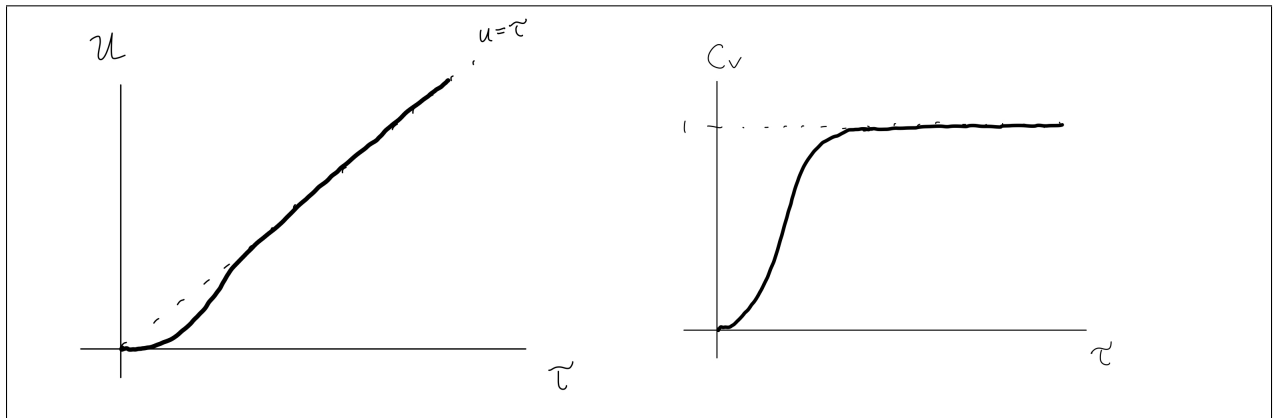$$= \frac{6\epsilon_0}{e^{2\epsilon_0/\tau} + 3}.$$

The heat capacity is then

$$C_V = (\partial U/\partial \tau)_V = -\frac{6\epsilon_0(-2\epsilon_0/\tau^2)e^{2\epsilon_0/\tau}}{(e^{2\epsilon_0/\tau} + 3)^2}$$
$$= \frac{12\epsilon_0^2}{\tau^2} \frac{e^{2\epsilon_0/\tau}}{(e^{2\epsilon_0/\tau} + 3)^2}$$

(e): 1 point

Sketch the behavior of $U(\tau)$ and $C(\tau)$, showing the limiting behaviors for $\tau \to \infty$ and $\tau \to 0$.

Problem 2

Adapted from Kittel & Kroemer, Chapter 3, problem 11 [One-dimensional gas]: 3 points

Consider an ideal gas of N particles, each of mass M, confined to a one-dimensional line of length L. Find the entropy at temperature τ. The particles have spin zero. [Note: treat the ideal gas as being in thermal contact with a reservoir at temperature τ. This is a quantum mechanics problem—try to follow the 3-dimensional version that we treated in class and in the book.]

The time-independent Schrodinger equation in 1D for a free particle is

$$-\frac{\hbar^2}{2M}\frac{d^2}{dx^2}\psi = E\psi.$$

If we choose the boundary conditions $\psi(0) = \psi(L) = 0$, this has solutions

$$\psi(x) = A\sin(n\pi x/L),$$

with $E = \frac{\hbar^2 \pi^2 n^2}{2ML^2}$, $n = 1, 2, 3, \ldots$. The partition function for a single particle is then

$$Z_1 = \sum_n e^{-\frac{\hbar^2 \pi^2 n^2}{2ML^2 \tau}}.$$

If τ is large enough, we can approximate the sum as an integral. In this case it is simply a one-dimensional integral, so $\sum_n \to \int_0^\infty dn$. Thus

$$Z_1 = \int_0^\infty dn\, e^{-\frac{\hbar^2 \pi^2 n^2}{2ML^2 \tau}}.$$

If we define $x \equiv \pi\hbar n/L\sqrt{2M\tau}$, this becomes

$$Z_1 = \frac{L\sqrt{2M\tau}}{\pi\hbar} \int_0^\infty dx\, e^{-x^2}.$$

This Gaussian integral has the value $\sqrt{\pi}/2$. Thus

$$Z_1 = \frac{L}{\hbar}\sqrt{\frac{M\tau}{2\pi}}.$$

For a gas of N indistinguishable particles, we will consider the classical regime in which the partition function can be written $Z_N = (Z_1)^N/N!$, so that

$$\ln Z_N = N\ln Z_1 - \ln N!$$
$$= N\ln\left(\frac{L}{\hbar}\sqrt{\frac{M\tau}{2\pi}}\right) - \ln N!$$

Using Stirling's approximation, this becomes

$$\ln Z_N = N \ln(\frac{L}{\hbar}\sqrt{\frac{M\tau}{2\pi}}) - N \ln N + N$$

$$= N \ln(\frac{L}{N\hbar}\sqrt{\frac{M\tau}{2\pi}}) + N.$$

Finally, the entropy is

$$\sigma = \frac{\partial}{\partial\tau}(\tau \ln Z_N) = \ln Z_N + \tau\frac{\partial \ln Z_N}{\partial\tau}$$

$$= N \ln(\frac{L}{N\hbar}\sqrt{\frac{M\tau}{2\pi}}) + N + \tau\frac{N}{2\tau}$$

$$= N[\ln(\frac{L}{N\hbar}\sqrt{\frac{M\tau}{2\pi}}) + 3/2].$$

We recognize $n \equiv N/L$ as the particle density; then we can define the 1D "quantum concentration" $n_Q \equiv \sqrt{M\tau/2\pi\hbar^2}$ so that

$$\sigma = N[\ln(n_Q/n) + 3/2].$$

Problem 3

3 points

This problem will give you a better understanding of the "quantum concentration" used repeatedly in your textbook. The de Broglie wavelength λ for a particle with momentum p is defined as $\lambda = h/p$, where $h = 2\pi\hbar$ is Planck's constant. If we don't know the momentum, but we know that the particle is part of a gas at temperature τ, then we can define the "thermal de Broglie wavelength" λ_{th} by assuming that the kinetic energy of the particle is equal to $\frac{3}{2}\tau$, as we derived in class. Derive an expression for the thermal de Broglie wavelength in terms of $\hbar$, τ, the particle mass m, and some numerical constants. What is the concentration n of the gas if the average spacing between particles equals λ_{th}? (Hint: n has units of inverse volume.) Compare your answer with the definition of the quantum concentration n_Q given in the book. The two formulas should differ only by a numerical constant. Evaluate the ratio n/n_Q.

If the average kinetic energy of the particle is $\frac{3}{2}\tau$, then since $KE = p^2/2m$, we can see that the thermal average momentum should be $\sqrt{(2m)(3\tau/2)} = \sqrt{3m\tau}$. Then the thermal de Broglie wavelength should be

$$\lambda_{th} = 2\pi\hbar/\sqrt{3m\tau}.$$

If the average spacing between particles is λ_{th}, the concentration should be 1 particle per λ_{th}^3 of volume; that is,

$$n = \frac{1}{\lambda_{th}^3} = \frac{(3m\tau)^{3/2}}{(2\pi\hbar)^3} = \left(\frac{3m\tau}{4\pi^2\hbar^2}\right)^{3/2}.$$

$\square$

The definition of quantum concentration given in the book is $n_Q \equiv (m\tau/2\pi\hbar^2)^{3/2}$. Thus

$$\frac{n}{n_Q} = \frac{\left(\frac{3m\tau}{4\pi^2\hbar^2}\right)^{3/2}}{(m\tau/2\pi\hbar^2)^{3/2}} = (3/2\pi)^{3/2} \approx 0.33.$$

So these definitions are very similar. The "quantum concentration" is the concentration that particles would have if they were packed to within an average separation of 1 thermal de Broglie wavelength from each other. It is at this distance that the "quantum waviness" of the particles becomes important.

Problem 4

Before it was understood that particles, even in the classical regime, are indistinguishable (a revelation of quantum physics), the statistical treatment of the ideal gas of N non-interacting particles gives a partition function $Z_N = (Z_1)^N$, where Z_1 is the partition function of a single particle (as opposed to $Z_N = (Z_1)^N/N!$, which takes the particles' indistinguishability into account in the classical regime). Let's feign ignorance for a moment, and see what the differences are between the predictions of these two models. For both, let's use the partition function for a single particle that we have derived in class, $Z_1 = n_Q V$, where $n_Q \equiv \left(\frac{m\tau}{2\pi\hbar^2}\right)^{3/2}$.

(a): 1 point

Calculate the entropy for an ideal gas of N particles, *ignoring the indistinguishability of particles*, i.e. start with the partition function $Z_N = (Z_1)^N$.

> We can calculate:
>
> $$\begin{aligned} \sigma = (\partial(\tau \ln Z_N)/\partial\tau) &= \ln Z_N + \tau\partial\ln Z_N/\partial\tau \\ &= N\ln Z_1 + N\tau\partial\ln Z_1/\partial\tau \\ &= N\ln(n_Q V) + \frac{3}{2}N \\ &= N[\ln(n_Q V) + \frac{3}{2}] \end{aligned}$$

(a): 1 point

(b): 1 point

Show that the entropy derived in part (a) is not extensive. This is the "Gibbs Paradox". (Reminder: if you double N and V for the system, an extensive quantity should also double).

> Let's calculate:
>
> $$\frac{\sigma(2N, 2V)}{\sigma(N, V)} = \frac{2N[\ln(2n_Q V) + \frac{3}{2}]}{N[\ln(n_Q V) + \frac{3}{2}]}.$$
>
> If the entropy were extensive, we should expect this ratio to be 2, i.e. the entropy should double when N and V double. We can see that this expression for the entropy is not extensive.

(b): 1 point

(c): 1 point

Show that the Sackur-Tetrode equation for the ideal gas entropy, which takes into account the indistinguishability of the particles, gives an entropy that is extensive.

> The Sackur-Tetrode equation for the entropy is
>
> $$\sigma = N[\ln(n_Q V/N) + \frac{5}{2}].$$
>
> We can evaluate:
>
> $$\frac{\sigma(2N, 2V)}{\sigma(N, V)} = \frac{2N[\ln(2n_Q V/2N) + \frac{5}{2}]}{N[\ln(n_Q V/N) + \frac{5}{2}]} = 2.$$
>
> Thus the entropy given by the Sackur-Tetrode equation is extensive, resolving the Gibbs paradox.

(c): 1 point