PHYS 301: Thermodynamics and Statistical Mechanics
Solutions to Problem Set #7

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Question 1: Partition Function of a General Gas Molecule

We are given the single-molecule partition function as a product of its translational, rotational, vibrational, and electronic components. With $Z_e = 1$, the partition function is:

$$Z_1 = Z_{\text{trans}} Z_{\text{rot}} Z_{\text{vib}} \tag{1}$$

For a gas of N indistinguishable molecules, the total partition function is:

$$Z_N = \frac{(Z_1)^N}{N!} = \frac{(Z_{\text{trans}} Z_{\text{rot}} Z_{\text{vib}})^N}{N!} \tag{2}$$

The average internal energy of the system is given by $\langle E \rangle = -\frac{\partial \ln Z_N}{\partial \beta}$. Taking the natural logarithm of Z_N:

$$\begin{aligned} \ln Z_N &= N \ln(Z_{\text{trans}} Z_{\text{rot}} Z_{\text{vib}}) - \ln(N!) \\ &= N \ln Z_{\text{trans}} + N \ln Z_{\text{rot}} + N \ln Z_{\text{vib}} - \ln(N!) \end{aligned} \tag{3}$$

Because the derivative operator is linear, the total average energy is simply the sum of the average energies of the individual modes:

$$\langle E \rangle = \langle E_{\text{trans}} \rangle + \langle E_{\text{rot}} \rangle + \langle E_{\text{vib}} \rangle \tag{4}$$

where $\langle E_{\text{mode}} \rangle = -N \frac{\partial \ln Z_{\text{mode}}}{\partial \beta}$. We will compute these term by term.

(a) Compute the average energy $\langle E \rangle$ in the high-temperature limit

1. Translational Energy: We know that $Z_{\text{trans}} = \frac{V}{\lambda_Q^3}$, where the thermal de Broglie wavelength is $\lambda_Q = \frac{h}{\sqrt{2\pi m k_B T}} \propto \beta^{1/2}$. Thus, $Z_{\text{trans}} \propto \beta^{-3/2}$, which implies:

$$\ln Z_{\text{trans}} = -\frac{3}{2} \ln \beta + \text{terms independent of } \beta \tag{5}$$

Taking the derivative:

$$\langle E_{\text{trans}} \rangle = -N \frac{\partial}{\partial \beta} \left(-\frac{3}{2} \ln \beta \right) = \frac{3N}{2\beta} = \frac{3}{2} N k_B T \tag{6}$$

2. Rotational Energy: The given rotational partition function in the high-temperature limit ($k_B T \gg \epsilon$) is:

$$Z_{\text{rot}} \approx \frac{k_B T}{\epsilon} = \frac{1}{\beta \epsilon} \tag{7}$$

$$\ln Z_{\text{rot}} = -\ln\beta - \ln\epsilon \tag{8}$$

Taking the derivative:

$$\langle E_{\text{rot}}\rangle = -N\frac{\partial}{\partial\beta}(-\ln\beta) = \frac{N}{\beta} = Nk_BT \tag{9}$$

3. Vibrational Energy: The vibrational partition function is given as:

$$Z_{\text{vib}} = \frac{e^{-\beta\hbar\omega/2}}{1-e^{-\beta\hbar\omega}} \tag{10}$$

$$\ln Z_{\text{vib}} = -\frac{\beta\hbar\omega}{2} - \ln(1-e^{-\beta\hbar\omega}) \tag{11}$$

Taking the derivative:

$$\begin{aligned}\langle E_{\text{vib}}\rangle &= -N\frac{\partial}{\partial\beta}\left[-\frac{\beta\hbar\omega}{2} - \ln(1-e^{-\beta\hbar\omega})\right]\\ &= N\left[\frac{\hbar\omega}{2} + \frac{1}{1-e^{-\beta\hbar\omega}}(-e^{-\beta\hbar\omega})(-\hbar\omega)\right]\\ &= N\left[\frac{\hbar\omega}{2} + \frac{\hbar\omega}{e^{\beta\hbar\omega}-1}\right]\end{aligned} \tag{12}$$

Now, we apply the high-temperature limit ($k_BT \gg \hbar\omega$, which means $\beta\hbar\omega \ll 1$). We can Taylor expand the exponential term in the denominator: $e^{\beta\hbar\omega} \approx 1 + \beta\hbar\omega$.

$$\begin{aligned}\langle E_{\text{vib}}\rangle &\approx N\left[\frac{\hbar\omega}{2} + \frac{\hbar\omega}{1+\beta\hbar\omega-1}\right]\\ &= N\left[\frac{\hbar\omega}{2} + \frac{\hbar\omega}{\beta\hbar\omega}\right]\\ &= N\left(\frac{\hbar\omega}{2} + k_BT\right) \approx Nk_BT \quad \text{for} \quad k_BT \gg \hbar\omega.\end{aligned} \tag{13}$$

Total Average Energy: Summing the three contributions together:

$$\begin{aligned}\langle E\rangle &= \frac{3}{2}Nk_BT + Nk_BT + Nk_BT\\ &= Nk_BT\left(\frac{3}{2}+1+1\right)\end{aligned} \tag{14}$$

$$\boxed{\langle E\rangle = \frac{7}{2}Nk_BT} \tag{15}$$

Physical interpretation: According to the Equipartition Theorem, each quadratic degree of freedom contributes $\frac{1}{2}k_BT$ to the energy. Our result shows 3 translational degrees ($\frac{3}{2}k_BT$), 2 rotational degrees (k_BT, typical for a linear molecule), and 2 vibrational degrees (kinetic and potential energy of the oscillator, contributing k_BT).

(b) Compute the heat capacity C_V in the high-temperature limit

The heat capacity at constant volume is defined as the temperature derivative of the average internal energy:

$$C_V = \left(\frac{\partial \langle E \rangle}{\partial T}\right)_V \tag{16}$$

Substituting our result from part (a):

$$C_V = \frac{\partial}{\partial T}\left(\frac{7}{2}Nk_BT\right) \tag{17}$$

So we obtain

$$\boxed{C_V = \frac{7}{2}Nk_B} \tag{18}$$

This recovers the classical equipartition limit for the heat capacity of a diatomic or linear polyatomic gas at high temperatures where all translational, rotational, and vibrational modes are fully accessible.

(c) Compute the average energy $\langle E \rangle$ and heat capacity C_V in the low-temperature limit

In the low-temperature limit, we assume that the thermal energy is much smaller than the spacing between the quantum energy levels for both rotation and vibration: $k_BT \ll \epsilon$ and $k_BT \ll \hbar\omega$. (Equivalently, $\beta\epsilon \gg 1$ and $\beta\hbar\omega \gg 1$).

We will compute the contributions to the energy mode by mode.

1. Translational Energy: The translational energy levels of a macroscopic box are incredibly close together, so even at very low temperatures, they can be treated continuously. Thus, the equipartition result still holds:

$$\langle E_{\text{trans}} \rangle = \frac{3}{2}Nk_BT \tag{19}$$

2. Rotational Energy: In the low-temperature limit, we cannot use the continuous integral approximation for the rotational partition function. We must look at the first few terms of the discrete sum:

$$\begin{aligned} Z_{\text{rot}} &= \sum_{j=0}^{\infty}(2j+1)e^{-\beta j(j+1)\epsilon} \\ &= 1 + 3e^{-2\beta\epsilon} + 5e^{-6\beta\epsilon} + \dots \end{aligned} \tag{20}$$

For $\beta\epsilon \gg 1$, the exponential terms are extremely small. We can approximate $\ln Z_{\text{rot}}$ using $\ln(1+x) \approx x$:

$$\ln Z_{\text{rot}} \approx \ln(1 + 3e^{-2\beta\epsilon}) \approx 3e^{-2\beta\epsilon} \tag{21}$$

The average rotational energy is:

$$\langle E_{\text{rot}} \rangle = -N\frac{\partial \ln Z_{\text{rot}}}{\partial \beta} \approx -N\frac{\partial}{\partial \beta}(3e^{-2\beta\epsilon}) = 6N\epsilon e^{-2\beta\epsilon} \tag{22}$$

As $T \to 0$ ($\beta \to \infty$), this term vanishes exponentially. $\langle E_{\text{rot}} \rangle \to 0$.

3. Vibrational Energy: Using the exact expression for the vibrational energy derived in part (a):

$$\langle E_{\text{vib}} \rangle = N \left[\frac{\hbar\omega}{2} + \frac{\hbar\omega}{e^{\beta\hbar\omega} - 1} \right] \tag{23}$$

For $\beta\hbar\omega \gg 1$, the denominator $e^{\beta\hbar\omega} - 1 \approx e^{\beta\hbar\omega}$, which makes the thermal excitation term exponentially small ($\hbar\omega e^{-\beta\hbar\omega}$). As $T \to 0$, all molecules drop to the ground state, leaving only the zero-point energy:

$$\langle E_{\text{vib}} \rangle \to N\frac{\hbar\omega}{2} \tag{24}$$

Total Average Energy: Adding the non-vanishing terms together, the total average energy in the low-temperature limit is:

$$\boxed{\langle E \rangle \approx \frac{3}{2}Nk_BT + N\frac{\hbar\omega}{2}} \tag{25}$$

Heat Capacity: Taking the temperature derivative to find the heat capacity:

$$C_V = \left(\frac{\partial \langle E \rangle}{\partial T} \right)_V = \frac{\partial}{\partial T} \left(\frac{3}{2}Nk_BT + N\frac{\hbar\omega}{2} \right) \tag{26}$$

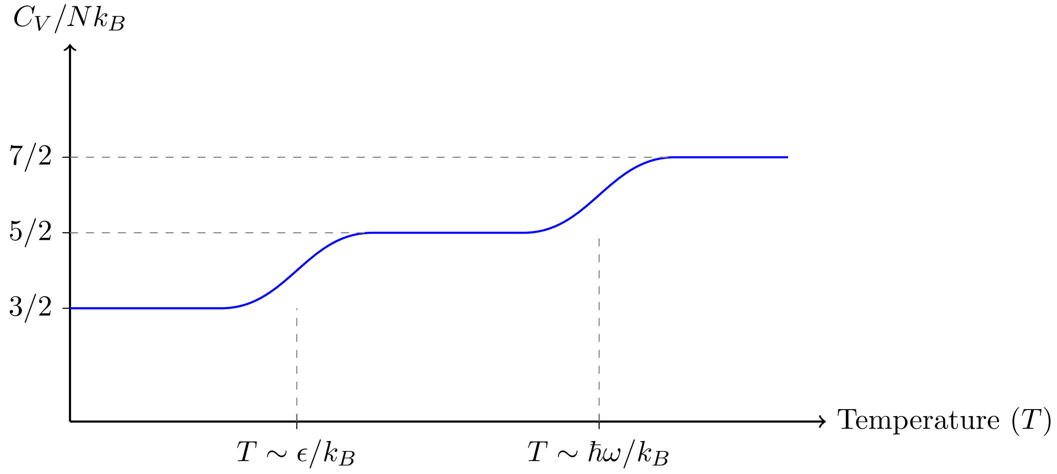
$$\boxed{C_V = \frac{3}{2}Nk_B} \tag{27}$$

Comparison and Physical Explanation: Both the average energy and the heat capacity are **smaller** in the low-temperature limit compared to the high-temperature limit. This happens because at low temperatures, the thermal energy (k_BT) is too small to bridge the discrete energy gaps required to excite the molecules into higher rotational or vibrational states. These degrees of freedom are quantum-mechanically "frozen out." Because they cannot absorb thermal energy, they do not contribute to the heat capacity, leaving only the translational degrees of freedom active.

(d) Sketch of the Heat Capacity $C_V/(Nk_B)$

Assuming $\hbar\omega \gg \epsilon$, the rotational modes will "unfreeze" (become thermally active) at a much lower temperature than the vibrational modes.

- **Low T ($k_BT \ll \epsilon$):** Only translation is active. $C_V/Nk_B = 3/2$.
- **Intermediate T ($\epsilon \ll k_BT \ll \hbar\omega$):** Translation and rotation are active. $C_V/Nk_B = 3/2 + 2/2 = 5/2$.
- **High T ($k_BT \gg \hbar\omega$):** Translation, rotation, and vibration are active. $C_V/Nk_B = 5/2 + 2/2 = 7/2$.


C_V/Nk_B
$7/2$
$5/2$
$3/2$
Temperature (T)
$T \sim \epsilon/k_B$
$T \sim \hbar\omega/k_B$