

Problem set 5

①

① a) The free energy F can be found using

$$F = -\tau \ln Z \quad (\text{see lecture 7})$$

where $\tau = k_B T$.

Therefore we need to find Z first.

From the definition of the partition function Z :

$$Z = \sum_s e^{-E_s/\tau} = \underbrace{1}_{E_s=0} + \underbrace{e^{-E/\tau}}_{E_s=E}$$

over two states

$$\therefore F = -\tau \ln(1 + e^{-E/\tau})$$

$$F = -k_B T \ln(1 + e^{-E/k_B T})$$

b) The entropy is found from

$$S = -\left(\frac{\partial F}{\partial T}\right)_V = \frac{\partial}{\partial T} \left[k_B T \ln(1 + e^{-E/k_B T}) \right] \quad (\text{at const. } V)$$

$$= k_B \ln(1 + e^{-E/k_B T}) + \frac{k_B T \left(-\frac{E}{k_B}\right) \left(-\frac{1}{T^2}\right) e^{-E/k_B T}}{1 + e^{-E/k_B T}}$$

$$= k_B \ln(1 + e^{-E/k_B T}) + \frac{E e^{-E/k_B T}}{T (1 + e^{-E/k_B T})}$$

$$S = k_B \ln(1 + e^{-E/k_B T}) + \frac{E}{T (e^{E/k_B T} + 1)}$$

U can be found using the definition of $F = U - TS \Rightarrow U = F + TS$ (because we have already calculated F and S)

$$\therefore U = -k_B T \ln(1 + e^{-E/k_B T}) + k_B T \ln(1 + e^{-E/k_B T}) + \frac{E}{e^{E/k_B T} + 1}$$

Or, directly from its definition:

$$U = \sum_s E_s P(E_s) = \frac{1}{Z} \sum_s E_s e^{-E_s/k_B T} = \frac{0 \cdot e^{-0/k_B T} + E e^{-E/k_B T}}{1 + e^{-E/k_B T}} = \frac{E}{e^{E/k_B T} + 1}$$

Thus

$$U = \frac{E}{e^{E/k_B T} + 1}$$

U is always smaller than E , and even smaller than $E/2$. U approaches $E/2$ in the high- T limit

$$U \xrightarrow{T \rightarrow \infty} \frac{E}{2} \quad \text{as } e^{E/k_B T} \xrightarrow{T \rightarrow \infty} 1$$

($e^0 \rightarrow 1$)

(3)

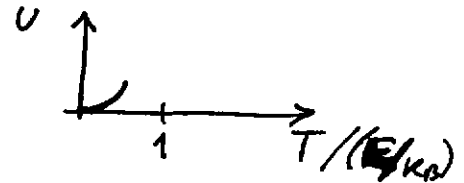
Move on the behaviour of U .

$$U = \frac{E}{e^{E/k_B T} + 1}$$

* Low temperature limit $k_B T \ll E$: ($e^{E/k_B T} \gg 1$)

$$U \approx \frac{E}{e^{E/k_B T}} = E e^{-E/k_B T} \xrightarrow{T \rightarrow 0} 0$$

- approaches zero exponentially fast

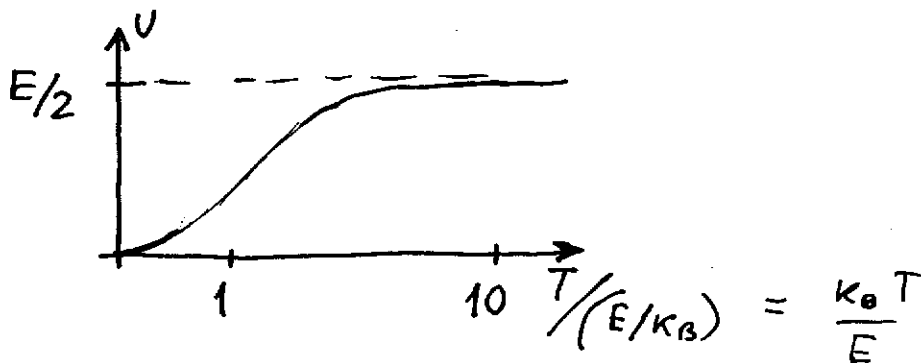


* High temperature limit $k_B T \gg E$

Then $\frac{E}{k_B T} \ll 1$, expand $e^{\frac{E}{k_B T}} \approx 1 + \frac{E}{k_B T} + \dots$

$$\therefore U \approx \frac{E}{2 + \frac{E}{k_B T}} \xrightarrow{T \rightarrow \infty} \frac{E}{2}$$

U approaches a constant value $E/2$ as $T \rightarrow \infty$



(2) One-dimensional gas.

Energy eigenvalues for a particle in a 1D box:

$$E_n = \frac{\hbar^2}{2m} \left(\frac{\pi}{L} \right)^2 n^2, \text{ where } n=1, 2, 3, \dots$$

in one dimension (1D)

To find U , need to find the partition function Z first.

$$Z_N = \frac{1}{N!} (Z_1)^N \quad - \text{for a classical ideal gas.}$$

One particle partition function:

$$Z_1 = \sum_{n=1}^{\infty} e^{-E_n/k_B T}$$

Can calculate this (as in lecture 8 for a 3D gas) by approximating the sum over n by a continuous integral

$$\begin{aligned} Z_1 &= \sum_{n=1}^{\infty} e^{-E_n/k_B T} \longrightarrow \approx \int_0^{\infty} dn e^{-E_n/k_B T} \\ &= \int_0^{\infty} dn e^{-\frac{\hbar^2}{2m} \left(\frac{\pi}{L} \right)^2 n^2 / k_B T} \\ &= \left(\frac{2m k_B T}{\hbar^2} \right)^{1/2} \left(\frac{L}{\pi} \right) \cdot \underbrace{\int_0^{\infty} dx e^{-x^2}}_{\text{Gaussian integral} = \frac{\sqrt{\pi}}{2}} \end{aligned}$$

define $x \equiv \sqrt{\frac{\hbar^2}{2m k_B T} \left(\frac{\pi}{L} \right)^2} n$

$$\therefore Z_1 = \frac{L}{\pi} \left(\frac{2m k_B T}{\hbar^2} \right)^{1/2} \frac{\sqrt{\pi}}{2} =$$

$$= L \cdot \underbrace{\left(\frac{m k_B T}{2\pi \hbar^2} \right)^{1/2}}_{\text{can be defined as}} = L \cdot n_Q^{(1D)}$$

can be defined as
quantum concentration in 1D
 $n_Q^{(1D)}$ — number of particles per
unit length
(instead of per unit
volume in 3D)

Z_1 — is dimensionless (has no units)

$L \cdot n_Q^{(1D)}$ is also dimensionless as
 $n_Q^{(1D)}$ has units of $[m^{-1}]$

Thus

$$n_Q^{(1D)} \equiv \left(\frac{m k_B T}{2\pi \hbar^2} \right)^{1/2}$$

— following the
analogy with 3D
from lecture notes
(lecture 8)

Thus $Z_1 = L \cdot n_Q^{(1D)}$, and therefore

$$Z_N = \frac{1}{N!} (Z_1)^N = \frac{1}{N!} (L \cdot n_Q^{(1D)})^N$$

$$Z_N = \frac{1}{N!} \left[\frac{L}{\hbar} \left(\frac{m k_B T}{2\pi} \right)^{1/2} \right]^N$$

U can be found using :

$$U = \tau^2 \frac{\partial [\ln Z_N]}{\partial \tau} = \tau^2 \frac{\partial}{\partial \tau} \ln \left[\frac{1}{N!} \left(\frac{L}{h} \left(\frac{m\tau}{2\pi} \right)^{1/2} \right)^N \right]$$

$$= \tau^2 \frac{1}{\frac{1}{N!} \left(\frac{L}{h} \left(\frac{m\tau}{2\pi} \right)^{1/2} \right)^N} \cdot \frac{\partial}{\partial \tau} \left[\frac{1}{N!} \left(\frac{L}{h} \right)^N \left(\frac{m\tau}{2\pi} \right)^{N/2} \right]$$

$$= \tau^2 \frac{1}{\frac{1}{N!} \left(\frac{L}{h} \right)^N \left(\frac{m\tau}{2\pi} \right)^{N/2}} \cdot \frac{1}{N!} \left(\frac{L}{h} \right)^N \cdot \left(\frac{m}{2\pi} \right)^{N/2} \frac{\partial}{\partial \tau} (\tau^{N/2})$$

$$= \tau^2 \frac{1}{\tau^{N/2}} \cdot \frac{N}{2} \cdot \tau^{\frac{N}{2}-1} = \frac{N}{2} \tau$$

Thus

$$U = \frac{N}{2} k_B T$$

- consistent with the equipartition theorem : each degree of freedom gives a contribution of $\frac{1}{2} k_B T$ to the thermal average internal energy of the system at sufficiently high temperatures. Here the gas is in the classical regime, i.e. at high temperature.

In 1D, each particle has one degree of freedom in their translational motion, therefore $\frac{1}{2} k_B T$. N particles (independent) will give $N \times \frac{1}{2} k_B T$, which is our result.

U can be also calculated using

$U = N U_1$ since the number of particles, canonical ensemble

N is given (fixed) and they are independent (ideal gas). U_1 is the average energy of a single particle, and can be calculated directly from the definition of U_1

$$U_1 = \frac{\sum_{n=0}^{\infty} E_n e^{-E_n/\tau}}{Z_1}$$

Here Z_1 is from page 5: $Z_1 = L \cdot n_Q^{(1D)}$

$$U_1 = \frac{1}{Z_1} \sum_{n=0}^{\infty} E_n e^{-E_n/\tau} \longrightarrow \approx \frac{1}{Z_1} \int_0^{\infty} dn E_n e^{-E_n/\tau}$$

$$= \frac{1}{Z_1} \int_0^{\infty} dn \cdot \frac{\hbar^2}{2m} \left(\frac{\pi}{L}\right)^2 n^2 e^{-\frac{\hbar^2}{2m} \left(\frac{\pi}{L}\right)^2 n^2 / k_B T}$$

(8)

$$= \frac{1}{Z_1} \frac{\hbar^2}{2m} \left(\frac{\pi}{L}\right)^2 \int_0^\infty dn \, n^2 e^{-a^2 n^2}$$

where we have introduced $a^2 \equiv \frac{\hbar^2}{2m} \left(\frac{\pi}{L}\right)^2 \cdot \frac{1}{k_B T}$

$$a \equiv \left[\frac{\hbar^2}{2m} \left(\frac{\pi}{L}\right)^2 \frac{1}{k_B T} \right]^{1/2}$$

Use the following integral

$$\left(\int_0^\infty dx \, x^2 e^{-a^2 x^2} = \frac{\sqrt{\pi}}{4a^3} \right) \quad (a > 0)$$

- integrals like this will be provided during the exam.

Thus :

$$U_1 = \frac{1}{Z_1} \frac{\hbar^2}{2m} \left(\frac{\pi}{L}\right)^2 \cdot \frac{\pi^{1/2}}{4 \left[\frac{\hbar^2}{2m} \left(\frac{\pi}{L}\right)^2 \frac{1}{k_B T} \right]^{3/2}}$$

substitute Z_1

$$= \frac{1}{L \cdot \left(\frac{m k_B T}{2\pi \hbar^2}\right)^{1/2}} \cdot \frac{\hbar^2 \pi^2 \pi^{1/2}}{2m \cdot L^2 \cdot 4 \left[\frac{\hbar^2}{2m} \left(\frac{\pi}{L}\right)^2 \frac{1}{k_B T} \right]^{3/2}}$$

$$= \frac{\cancel{\hbar^2}^2 \cancel{\pi}^{3/2} 2^{1/2} \cancel{\pi}^{1/2} \cancel{\hbar} \cdot 2^{3/2} \cancel{m}^{3/2} \cancel{L}^3 (k_B T)^{3/2}}{\cancel{L} \cdot \cancel{m}^{1/2} (k_B T)^{1/2} \cdot \cancel{2} \cancel{m} \cdot \cancel{L}^2 \cdot 4 \cdot \cancel{\hbar}^3 \cancel{\pi}^3}$$

$$= \frac{1}{2} k_B T \quad \text{Thus} \quad \boxed{U_1 = \frac{1}{2} k_B T} \Rightarrow \boxed{U = \frac{N}{2} k_B T}$$

3. Entropy of mixing

Since m and T are the same for the two gases, n_a is also the same.

Since the volumes $V_A = V_B \equiv V$ and $N_A = N_B \equiv N$ is also the same, the two gases have the same entropies before and after the wall is removed, and therefore the initial and final entropies

~~are~~ are equal $S_A^{(i)} = S_B^{(i)}$ and

$$S_A^{(f)} = S_B^{(f)}$$

The initial entropies have to be calculated at volume V and the number of particles N , for the two systems:

$$S_A^{(i)}(T, N, V), \quad S_B^{(i)}(T, N, V).$$

The final entropies have to be calculated at twice larger volumes, since the gases have expanded into the entire (combined) volume $2V$. Therefore, we have to apply the formula for the entropy at $2V$ for both gases: $S_A^{(f)}(T, N, 2V), S_B^{(f)}(T, N, 2V)$.

The total initial entropy (as extensive quantity)

is

$$S_{\text{total}}^{(i)} = S_A^{(i)}(T, N, V) + S_B^{(i)}(T, N, V).$$

$$= 2 S_A^{(i)}(T, N, V)$$

Similarly, the final ^{total} entropy is:

$$\begin{aligned} S_{\text{total}}^{(f)} &= S_A^{(f)}(T, N, \underline{2V}) + S_B^{(f)}(T, N, 2V) \\ &= 2 S_A^{(f)}(T, N, 2V) \end{aligned}$$

The change in the ~~ent~~ total entropy is

$$\Delta S = S_{\text{total}}^{(f)} - S_{\text{total}}^{(i)} = 2 S_A^{(f)}(T, N, 2V) - 2 S_A^{(i)}(T, N, V)$$

Applying the given formula we obtain:

$$\begin{aligned} \Delta S &= 2 \left[k_B N \left(\ln \frac{2V n_Q}{N} + \frac{5}{2} \right) - k_B N \left(\ln \frac{V n_Q}{N} + \frac{5}{2} \right) \right] \\ &= 2 k_B N \left[\ln \frac{2V n_Q}{N} - \ln \frac{V n_Q}{N} \right] \\ &= 2 k_B N \ln \frac{2V n_Q}{N \cdot \frac{V n_Q}{N}} = \\ &= 2 k_B N \ln 2 \end{aligned}$$

Thus $\Delta S = 2 k_B N \ln 2$

④ Harmonic oscillator in the canonical formalism.

- (a) The partition function Z has already been found in problem 3 of Problem Set 3 :

$$Z = \frac{1}{1 - e^{-\hbar\omega/k_B T}}$$

- (b) The free energy F is found from Z using

$$F = -k_B T \ln Z \quad (\text{see Lecture 7})$$

$$= -k_B T \ln \frac{1}{1 - e^{-\hbar\omega/k_B T}}$$

$$= -k_B T \ln (1 - e^{-\hbar\omega/k_B T})^{-1} =$$

$$= k_B T \ln (1 - e^{-\hbar\omega/k_B T})$$

(c) The entropy S can be found

using

$$S = - \left(\frac{\partial F}{\partial T} \right)_V \quad (\text{see Lecture 7})$$

$$\therefore S = - \frac{\partial}{\partial T} \left[k_B T \ln(1 - e^{-\hbar\omega/k_B T}) \right]$$

$$= -k_B \ln(1 - e^{-\hbar\omega/k_B T}) - k_B T \frac{(-1) \left(-\frac{\hbar\omega}{k_B} \right) \left(-\frac{1}{T^2} \right) e^{-\hbar\omega/k_B T}}{1 - e^{-\hbar\omega/k_B T}}$$

$$= -k_B \ln(1 - e^{-\hbar\omega/k_B T}) + \frac{\hbar\omega e^{-\hbar\omega/k_B T}}{T (1 - e^{-\hbar\omega/k_B T})}$$

$$= \frac{\hbar\omega}{T (e^{\hbar\omega/k_B T} - 1)} - k_B \ln(1 - e^{-\hbar\omega/k_B T})$$

(d) Using the results for F and S , and the definition of $F = U - TS$, U can be found as

$$U = F + TS = \frac{\hbar\omega}{e^{\hbar\omega/k_B T} - 1}$$

(e) The heat capacity, from its definition $C_V = \left(\frac{\partial U}{\partial T} \right)_V$ is :

$$\begin{aligned}
 C_V &= \frac{\partial}{\partial T} \left(\frac{\hbar \omega}{e^{\hbar \omega / k_B T} - 1} \right) = \\
 &= \frac{-\hbar \omega \frac{\partial}{\partial T} (e^{\hbar \omega / k_B T} - 1)}{(e^{\hbar \omega / k_B T} - 1)^2} = \\
 &= \frac{-\hbar \omega \cdot \frac{\hbar \omega}{k_B} \left(-\frac{1}{T^2}\right) \cdot e^{\hbar \omega / k_B T}}{(e^{\hbar \omega / k_B T} - 1)^2} = k_B \left(\frac{\hbar \omega}{k_B T} \right)^2 \frac{e^{\hbar \omega / k_B T}}{(e^{\hbar \omega / k_B T} - 1)^2}
 \end{aligned}$$

Thus

$$C_V = k_B \left(\frac{\hbar \omega}{k_B T} \right)^2 \frac{e^{\hbar \omega / k_B T}}{(e^{\hbar \omega / k_B T} - 1)^2}$$

From the thermodynamic identity

$$dU = TdS - pdV, \text{ the definition of}$$

$$C_V = \left(\frac{\partial U}{\partial T} \right)_V \rightarrow \text{at constant } V \text{ implies}$$

that for such a process $dU = TdS$

and therefore $C_V = T \left(\frac{\partial S}{\partial T} \right)_V$. Differentiating

S (from (c)) with respect to T will give the same result as

5. Polymer system

- (a) Each link can point either left or right, so this system is the same as a collection of coins or a two-state paramagnet. The multiplicity is

$$g = \binom{N}{N_R} = \frac{N!}{N_R! (N - N_R)!}$$

So the entropy is

$$\begin{aligned} S &= k_B \ln g = k_B \ln \frac{N!}{N_R! (N - N_R)!} \\ &\approx k_B \left\{ N \ln N - N - (N_R \ln N_R - N_R) - [(N - N_R) \ln (N - N_R) - (N - N_R)] \right\} \\ &= N \ln N - N_R \ln N_R - (N - N_R) \ln (N - N_R). \end{aligned}$$

- (b) Each right-pointing link increases L by ℓ , while each left-pointing link decreases L by ℓ , so the net length must be

$$L = \ell (N_R - \underbrace{N_L}_{\substack{\text{the number of} \\ \text{left-pointing links}}}) = \ell (2N_R - N) \quad \text{or} \quad N_R = \frac{1}{2} \left(\frac{L}{\ell} + N \right)$$

If L is analogous to V and F is analogous to $-p$, then the thermodynamic identity ($dU = TdS - pdV$) should be

$$dU = TdS + FdL$$

The second term makes sense: It is the work (force times displacement) done on the system by quasistatically stretching it by an amount dL .

For a process in which $dU=0$, the thermodynamic identity says \rightarrow (constant U)

$$FdL = -TdS, \text{ or}$$

$$\boxed{F = -T \left(\frac{\partial S}{\partial L} \right)_U}$$

(c) To use $F = -T \left(\frac{\partial S}{\partial L} \right)_U$ we need to express our result for S in terms of L , using $N_R = \frac{1}{2} \left(\frac{L}{\ell} + N \right)$

or we can express the partial derivative $\frac{\partial S}{\partial L}$ in terms of N_R using the chain rule:

$$\frac{\partial S}{\partial L} = \frac{\partial S}{\partial N_R} \frac{\partial N_R}{\partial L} = \frac{\partial S}{\partial N_R} \cdot \frac{1}{2\ell}$$

Therefore, by the result of part (a),

$$F = -\frac{k_B T}{2\ell} \left[-\ln N_R - \frac{N_R}{N_R} + \ln(N - N_R) + \frac{N - N_R}{N - N_R} \right] =$$

$$= -\frac{k_B T}{2\ell} \ln \left(\frac{N - N_R}{N_R} \right)$$

Using $N_R = \frac{1}{2} \left(\frac{L}{\ell} + N \right)$, we can rewrite this in terms of L : $\Rightarrow \frac{N_R}{N} = \frac{1}{2} \left(\frac{L}{\ell N} + 1 \right)$

$$F = -\frac{k_B T}{2\ell} \ln \left(\frac{N}{N_R} - 1 \right) =$$

$$= -\frac{k_B T}{2\ell} \ln \left(\frac{2}{\frac{L}{\ell N} + 1} - 1 \right) =$$

$$= -\frac{k_B T}{2\ell} \ln \left(\frac{1 - \frac{L}{\ell N}}{1 + \frac{L}{\ell N}} \right) = \frac{k_B T}{2\ell} \ln \left(\frac{1 + L/\ell N}{1 - L/\ell N} \right)$$

$$F = \frac{k_B T}{2\ell} \ln \left(\frac{1 + \frac{L}{\ell N}}{1 - \frac{L}{\ell N}} \right)$$

(d) For $L \ll N\ell$, the argument of the logarithm is approximately

$$\frac{1 + \frac{L}{N\ell}}{1 - \frac{L}{N\ell}} \approx \left(1 + \frac{L}{N\ell}\right) \left(1 + \frac{L}{N\ell}\right) \quad \left[\text{using } \frac{1}{1-x} \approx 1+x+\dots \text{ for } x \ll 1 \right]$$

$$\approx 1 + \frac{2L}{N\ell} \quad \left[\text{up to the lowest order term in } \frac{L}{N\ell} \right]$$

Thus:

$$F \approx \frac{k_B T}{2\ell} \ln \left(1 + \frac{2L}{N\ell} \right)$$

$$\approx \frac{k_B T}{2\ell} \cdot \frac{2L}{N\ell} \quad \left(\text{using } \ln(1+x) \approx x + \dots \text{ for } x \ll 1 \right)$$

Therefore

$$\boxed{F \approx \frac{k_B T L}{N\ell^2}} \quad \text{for } L \ll N\ell$$

The expression is linear in L ; it has the form of Hooke's law, with the

"spring constant" equal to $\frac{k_B T}{N\ell^2}$

— increases with T .

So, the tension is proportional to T : it is greater at high temperature than at low T . For a given tension, increasing T should cause the rubber band to contract: L must decrease to compensate. Although this behavior is opposite to that of an ideal gas, it does make sense: at higher temperature there should be more randomness in the orientation of the links, causing the rubber band to contract.

⑥ Rotation of a diatomic molecule

- (a) The partition function for the rotational states of a molecule is

$$Z_R = \sum_s e^{-E_s/k_B T} \quad (\text{standard definition}).$$

Here, the \sum_s - is over all states.

To calculate the Z explicitly, we want to transform it to the sum over the given energy levels j (\sum_j), but upon doing so we need to take into account the multiplicity of each energy level.

To each energy level j (with the energy E_j which is given by

$$E_j = j(j+1) E_0, \text{ where we have introduced for notational simplicity } E_0 \equiv \frac{\hbar^2}{I})$$

there corresponds $g(j) = (2j+1)$ states.

[$(2j+1)$ -fold degenerate], i.e. the multiplicity of each energy level E_j is

$$g(j) = (2j+1). \quad \text{Therefore}$$

$$\begin{aligned} Z_R &= \sum_s e^{-E_s/k_B T} = \sum_{j=0}^{\infty} g(j) e^{-E_j/k_B T} \\ &= \sum_{j=0}^{\infty} (2j+1) e^{-j(j+1) E_0/k_B T} \end{aligned}$$

(b) For $T \gg \frac{\hbar^2}{I k_B} = \frac{E_0}{k_B}$, the conversion of the \sum_j into an integral $\int dj$ gives

$$Z_R \approx \int_0^{\infty} dj (2j+1) e^{-j(j+1) E_0/k_B T}$$

Define $x \equiv j(j+1) = j^2 + j$

Then $dx = d(j^2 + j) = 2j dj + dj = (2j+1) dj$

Therefore

$$Z_R \approx \int_0^{\infty} dx e^{-x E_0 / k_B T} = - \frac{k_B T}{E_0} e^{-x} \Big|_0^{\infty}$$

$$= \frac{k_B T}{E_0}$$

Thus

$$\boxed{Z_R \approx \frac{k_B T I}{\hbar^2}} \quad \text{for } T \gg \frac{\hbar^2}{I k_B}$$

(c) For $T \ll \frac{\hbar^2}{I k_B} \equiv \frac{E_0}{k_B}$, the first two terms give:

$$\boxed{Z_R \approx \underbrace{1}_{j=0} + \underbrace{3 e^{-2E_0/k_B T}}_{j=1}}$$

(d) For $T \gg \frac{\hbar^2}{I k_B} \equiv \frac{E_0}{k_B}$ ($Z_R = \frac{k_B T}{E_0}$),

$$U = \tau^2 \frac{\partial \ln Z_R}{\partial \tau} \quad \text{gives}$$

$$U = \tau^2 \frac{\partial}{\partial \tau} \left(\ln \frac{k_B T}{E_0} \right) = \tau^2 \frac{\partial}{\partial \tau} \left(\ln \frac{\tau}{E_0} \right) = \tau^2 \frac{1}{\tau/E_0} \cdot \frac{1}{E_0} = \tau$$

Thus

$$\boxed{U \approx k_B T} \quad \text{at high } T$$

$$(T \gg \frac{\hbar^2}{Ik_B})$$

- consistent with the equipartition theorem (2 rotational degrees of freedom, 2 angles needed to specify the orientation in 3D) : $2 \cdot \frac{1}{2} k_B T = k_B T$

$$C_V = \frac{\partial U}{\partial T} = k_B$$

At low temperatures $T \ll \frac{\hbar^2}{Ik_B} \equiv \frac{E_0}{k_B}$,

$$U = \tau^2 \frac{\partial \ln Z_R}{\partial \tau} \text{ gives}$$

$$U = \tau^2 \frac{\partial}{\partial \tau} \left[\ln (1 + 3e^{-2E_0/\tau}) \right] =$$

$$= \tau^2 \frac{3(-2E_0)(-\frac{1}{\tau^2})e^{-2E_0/\tau}}{1 + 3e^{-2E_0/\tau}} =$$

$$= \frac{6E_0 e^{-2E_0/\tau}}{1 + 3e^{-2E_0/\tau}} = \frac{6E_0}{e^{2E_0/\tau} + 3}$$

Here $\frac{E_0}{\tau} = \frac{E_0}{k_B T} \gg 1$, therefore $e^{3E_0/\tau} \gg 3$

$$\therefore U \approx \frac{6E_0}{e^{2E_0/\tau}} \xrightarrow{\tau \rightarrow 0} \frac{1}{\infty} \rightarrow 0$$

approaches zero exponentially fast, with $T \rightarrow 0$

$$\begin{aligned}
 C_v &= \frac{\partial U}{\partial T} \approx \frac{\partial}{\partial T} \left(\frac{6 E_0}{e^{2E_0/k_B T}} \right) \\
 &= 6 E_0 \frac{\partial}{\partial T} \left(e^{-2E_0/k_B T} \right) = 6 E_0 \left(-\frac{2E_0}{k_B} \right) \left(-\frac{1}{T^2} \right) e^{-2E_0/k_B T} \\
 &= 12 k_B \left(\frac{E_0}{k_B T} \right)^2 \frac{1}{e^{2E_0/k_B T}} \longrightarrow \frac{1}{\infty} \longrightarrow 0
 \end{aligned}$$

$C_v \rightarrow 0$ exponentially fast as $T \rightarrow 0$

sketches:

