1) (5') The spacing of particles should be larger than the characteristic length

$$\lambda = \frac{h}{\sqrt{2\pi m k T}}$$

so

$$n = \frac{N}{V} < \frac{1}{\lambda^3}$$

in the classical limit $h \to 0$ or at high temperature, the thermal wavelength becomes small compared to the interparticle spacing $n^{-1/3}$, which means that the effect of quantum diffraction and interference is negligible. As $T$ falls or $n$ rises, the quantum interference between nearby particles becomes crucial. It is also convenient to introduce the dimensionless phase space density $n\lambda^3$ which is small in the classical limit. When $n\lambda^3$ is order of unity, the ideal gas changes character. An ideal gas of fermions undergoes a crossover from classical ideal gas to a degenerate Fermi gas at the Fermi temperature $T_F$ given by the qualitative relation $n\lambda^3 \sim 1$. Equivalently, the ideal gas of bosons undergoes a sharp phase transition at a temperature $T_c$ by the same criterion.

Or, in mathematical way, the quantum gas pressure $P = nkT(1 - (-1)^{\text{species}} \lambda^3 n 2^{-5/2} + \cdots)$ (note that $\text{species} = 1$ for fermion and 0 for boson). This pressure can be derived by canonical formulation. Obviously, $n\lambda^3 << 1$ is necessary to disregard the quantum effect.

Or, consider the entropy $S = N k \ln \frac{e^V}{N!}$. The 3rd law of thermodynamics requires the $S_{T=0} = 0$. Therefore, the $n\lambda^3 \approx 1$ is the limit of classical mechanics. $n$ should be much smaller than $\lambda$ to ensure $S > 0$ for $T > 0$

2) (10'). The definition of partition function is

$$Z = \sum_{\mu} e^{-\beta \mathcal{H}}$$

where $\mu$ is the microstate. In this problem, the Hamiltonian is

$$\mathcal{H} = \mathcal{H}_{\text{translation}} + \mathcal{H}_{\text{rotation}} + \mathcal{H}_{\text{vibration}}$$

Therefore

$$Z = \sum_{\mu_{\text{translation}}} \sum_{\mu_{\text{rotation}}} \sum_{\mu_{\text{vibration}}} e^{-\beta (\mathcal{H}_{\text{translation}} + \mathcal{H}_{\text{rotation}} + \mathcal{H}_{\text{vibration}})}$$

$$= Z_{\text{translation}} Z_{\text{rotation}} Z_{\text{vibration}}$$

Therefore the free energy is

$$F = -kT \ln Z = -kT \ln (Z_{\text{translation}} Z_{\text{rotation}} Z_{\text{vibration}})$$

$$= -kT \ln Z_{\text{translation}} - kT \ln Z_{\text{rotation}} - kT \ln Z_{\text{vibration}}$$

$$= F_{\text{translation}} + F_{\text{rotation}} + F_{\text{vibration}}$$
The partition function the $Z_{\text{translation}}$

$$Z_{\text{translation}} = \int e^{-\beta \sum \frac{p_i^2}{2m}} \prod_i \frac{d^3p_i d^3q_i}{h^3 N!}$$

$$= V^N \left( \frac{2\pi m kT}{h^2} \right)^{3N/2}$$

$$= \frac{1}{N!} \left( \frac{V}{\lambda^3} \right)^N$$

where $\lambda$ has been defined above.

The rotational partition function $Z_{\text{rotation}}$ for the system is the $N$ power of single particle partition function $Z_{\text{rotation}}$

$$\tilde{Z}_{\text{rotation}} = \sum_{m=-\infty}^{\infty} e^{-\beta m^2 h^2 / 2T}$$

The vibrational partition function $Z_{\text{vibration}}$ for the system is the $N$ power of single particle partition function $Z_{\text{vibration}}$

$$\tilde{Z}_{\text{vibration}} = \sum_{n=0}^{\infty} e^{-\beta (n+\frac{1}{2})h\omega} = \frac{e^{\frac{1}{2} \beta h\omega}}{e^{\beta h\omega} - 1}$$

Therefore

$$Z_{\text{vibration}} = \left( \frac{e^{-\beta h\omega/2}}{1 - e^{-\beta h\omega}} \right)^N$$

3) (15’). The translational free energy is

$$F_{\text{translation}} = -kT \ln Z_{\text{translation}}$$

$$= -NkT \ln V + NkT \ln N - NkT - \frac{3N}{2} kT \ln \left( \frac{2\pi m kT}{h^2} \right)$$

$$= -NkT \left[ \ln \left( \frac{eV}{N} \right) + \frac{3}{2} \ln \left( \frac{2\pi m kT}{h^2} \right) \right] \propto N$$

The free energy is proportional to $N$, so it is extensive.

The contribution of translation to the specific heat is calculated from the energy

$$U_{\text{ideal}} = -\frac{\partial \ln Z_{\text{translation}}}{\partial \beta} = \frac{3N}{2} kT$$

Therefore

$$c_{\text{translation}} = 3Nk/2$$

This is from the 3 degree of freedom for each particle. Each with specific heat $k/2$

4) (30’).

a) As is stated before

$$F_{\text{rotation}} = -kT \ln Z_{\text{rotation}}$$

$$= -NkT \ln \left( \sum_{l=-\infty}^{\infty} e^{-\beta l^2 h^2 / 2T} \right)$$

$$= -NkT \ln \left( \sum_{l=-\infty}^{\infty} e^{-\beta \epsilon_{\text{rot}}^2 / 2T} \right)$$

where $\epsilon_{\text{rot}}$ is the rotational energy.
The free energy is proportional to \( N \) and it is extensive. where \( \theta_{\text{rot}} = \frac{k^2}{2I} \) is defined as the characteristic temperature for rotation. \( \theta_{\text{rot}}/T = \frac{k^2}{2I_T} \) is a dimensionless parameter.

b) 
\[
U = -\frac{\partial}{\partial \beta} \ln Z_{\text{rotation}} = \frac{Nh^2}{2T} \sum_l l^2 \exp(-\beta l^2 \hbar^2) \sum_l \exp(-\beta l^2 \hbar^2) 
\]

(24)

c) For low temperature, \( \beta \to \infty \) so only the first two terms inside the single particle partition function survives
\[
\hat{Z}_{\text{rotation}} = \sum_{l=-\infty}^{\infty} e^{-\beta l^2 \hbar^2} 
\]
\[
\approx 1 + 2e^{-\theta_{\text{rot}}/T} 
\]

(25)

(26)

Therefore
\[
U = -N \frac{\partial \ln \hat{Z}_{\text{rotational}}}{\partial \beta} \approx \frac{2N\theta k}{e^{\theta k\beta} + 2} 
\]
\[
\approx 2Nk\theta_{\text{rot}}e^{-\theta_{\text{rot}}/T} 
\]

(27)

(28)

d) The specific heat of rotational DOF at low temperature
\[
c_v = \frac{\partial U}{\partial T} 
\]
\[
= 2Nk^2 \frac{\theta_{\text{rot}}^2}{T^2} e^{-\theta_{\text{rot}}/T} 
\]

(29)

(30)

At low temperatures, the only contributions come from the kinetic energy of the center of mass, and the molecule behaves like monatomic particle.

e) Using the Poisson summation formula, we have
\[
\sum_{l=-\infty}^{\infty} e^{-\theta_{\text{rot}} l^2 / T} = \sum_{m=-\infty}^{\infty} \sqrt{\frac{T}{\theta_{\text{rot}}}} e^{-\pi^2 m^2 T / \theta_{\text{rot}}} 
\]

(31)

Differentiating it with respect to \( \theta_{\text{rot}}/T \)
\[
\sum_{l=-\infty}^{\infty} l^2 e^{-\theta_{\text{rot}} l^2 / T} = \sqrt{\frac{T}{\theta_{\text{rot}}^3}} \sum_{m=-\infty}^{\infty} \left( \frac{\pi^2 m^2 T}{\theta_{\text{rot}}} - 1/2 \right) e^{-\pi^2 m^2 T / \theta_{\text{rot}}} 
\]

(32)

At high temperature, \( T \to \infty \), any terms that is \( m \neq 0 \) tends to zero fastly. So
\[
U_{\text{rot}} = \frac{Nh^2}{2T} \sum_l l^2 e^{-l^2 T / \theta_{\text{rot}}} 
\]
\[
\approx \frac{Nh^2}{2T} \frac{T}{2\theta_{\text{rot}}} 
\]
\[
= \frac{1}{2} NkT 
\]

(33)

f) At high temperature, specific heat tends to a constant. The asymptotic value of specific heat at high temperature is the value \( Nk/2 \). The rotation has one degree of freedom in this question because the Hamiltonian is only for rotation along z axis, the specific heat is therefore of \( Nk/2 \). The translation has 3 degree of freedom, so the specific heat is three \( Nk/2 \).
5) (20'), a) As is calculated before
\[ Z_{\text{vibration}} = \sum_{n=0}^{\infty} \exp(-\beta(n + \frac{1}{2})\hbar\omega) = \frac{e^{\frac{1}{2}\beta\hbar\omega}}{e^{\beta\hbar\omega} - 1} \] (34)

The free energy from vibration is
\[ F_{\text{vibration}} = NkT \left( \frac{1}{2} \beta\hbar\omega + \ln(1 - e^{-\beta\hbar\omega}) \right) \] (36)

b) The internal energy is
\[ U_{\text{vibration}} = N \left( \frac{\hbar\omega}{2} + \frac{e^{-\beta\hbar\omega}\hbar\omega}{1 - e^{-\beta\hbar\omega}} \right) \] (37)

Take the derivative with respect to \( T \) we get the vibrational heat capacity
\[ c_{\text{vibration}} = Nk \left( \frac{\hbar\omega}{kT} \right)^2 \frac{e^{-\beta\hbar\omega}}{(1 - e^{-\beta\hbar\omega})^2} \] (38)
\[ = N \frac{\hbar^2\omega^2 \text{csch}^2 \left( \frac{\hbar\omega}{2kT} \right)}{4kT^2} \] (39)

where \( \text{csch}(z) = 2/(e^z - e^{-z}) \) is the hyperbolic cosecant function.

c) At low temperature \( kT << \hbar\omega \) (we have another dimensionless parameter \( \hbar\omega/(kT) \)), the vibration heat capacity reads
\[ c_{\text{vibration}} = N \frac{\hbar^2\omega^2}{e^{\hbar\omega/(kT)kT^2}} \] (40)

The vibrational heat capacity tends to zero at low temperature. The behavior is same to rotational case. In the low temperature, the energy is below the minimum to excite the ground state of vibration, we can view them as the monatomic molecules and the kinetic energy is considered only.

d) At high temperature the hyperbolic cosecant function \( \text{csch}(z) \approx 1/z \) by this approximation one can get the high temperature heat capacity
\[ c_{\text{vibration}} = N \left( \frac{2kT}{\hbar\omega} \right)^2 \frac{\hbar^2\omega^2}{(4kT^2)} = Nk \] (41)

The vibration has longitudinal and transverse modes. Therefore the DOF is two. The specific heat for each particle is therefore two of \( Nk/2 \).

6) (10') The total free energy is
\[ F = \frac{3NkT}{2} \ln \frac{2\pi MVkT}{\hbar^2} + kT \left( \frac{1}{2} \beta\hbar\omega + \ln(1 - e^{-\beta\hbar\omega}) \right) - kT \ln(\sum_l e^{-\beta l^2\hbar^2}) \] (42)

The entropy is expressed as
\[ S = Nk \left( \ln \frac{e^V}{N} + \frac{3}{2} \ln \frac{2\pi mkT}{\hbar^2} \right) + \frac{N\hbar\omega}{T(e^{\beta\hbar\omega} - 1)} - kN \log(1 - e^{-\beta\hbar\omega}) \]
\[ + Nk \ln(\sum_l e^{-\theta_{\text{rot}}l^2/T}) + Nk \frac{\sum_l l^2 e^{-l^2T/\theta_{\text{rot}}}}{e^{-l^2T/\theta_{\text{rot}}}} \] (43)
In the low temperature region $T \to 0$

a) The translational part of entropy has the asymptotic value of $\frac{3}{2}Nk\ln T$. This is actually wrong, because at low temperature, the ideal gas is no long described classically. The 3rd law of thermodynamics tells us the entropy must be zero, not infinity.

b) The rotational part of entropy has the asymptotic value of $2Nk\theta_{rot}e^{\theta_{rot}/T}/T \to 0$

c) The vibrational part of entropy at low temperature is $Nke^{-\hbar\omega/(kT)} \to 0$

In the high temperature region $T \to \infty$

a) The translational part of entropy has the asymptotic value of $\frac{3}{2}Nk\ln T$

b) The rotational part of entropy has the asymptotic value of $Nk\ln T/2$

c) The vibrational part of entropy at low temperature is $Nk\ln T$

At high temperature, the rotation and vibration has 1 and 2 degree of freedom respectively. This has the same behavior with the translational motion, except for the number of DOF.

7) (10') The total energy fluctuation

$$<\Delta U^2> = <U^2> - <U>^2 = \frac{1}{Z} \sum U^2e^{-\beta U} - \frac{1}{Z^2}(\sum Ue^{-\beta U})^2$$

(44)

$$= \frac{1}{Z} \left( \frac{\partial^2 Z}{\partial \beta^2} - \frac{1}{Z^2} \left( \frac{\partial Z}{\partial \beta} \right)^2 \right)$$

(45)

$$= \frac{\partial^2 \ln Z}{\partial \beta^2}$$

(46)

$$= \frac{\partial^2 \ln Z}{\partial \beta^2}$$

(47)

$$= kT^2C_v$$

(48)

For the system here,

$$<\Delta U^2> = \frac{3N}{2\beta^2} + N \left( \frac{\hbar^2}{2T} \right)^2 \left[ \sum_{l=-\infty}^{\infty} l^4 e^{-\theta_{rot}l^2/T} - \left( \sum_{l=-\infty}^{\infty} l^2 e^{-\theta_{rot}l^2/T} \right)^2 \right] + N \frac{\hbar^2\omega^2 e^{\beta \hbar \omega}}{(e^{\beta \hbar \omega} - 1)^2}$$

(49)