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Thermodynamics and Statistical Mechanics

Statistical Mechanics III

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- Statistical mechanics of harmonic oscillators
- Vibrational modes of diatomic molecules
- Rotational modes of diatomic molecules

HARMONIC OSCILLATORS

Consider an ensemble of N identical harmonic oscillators

each of them described by Hamiltonian ☛ $\hat{H} = \frac{\hat{p}^2}{2m} + \frac{kx^2}{2}$

Stationary Schrodinger equation becomes ↴

$$\left(- \frac{\hbar^2}{2m} \frac{d^2}{dx^2} + \frac{kx^2}{2} \right) \Psi(x) = \varepsilon \, \Psi(x) \qquad (52)$$

Boundary conditions $\Psi(\pm\infty) = 0$ and $\int_{-\infty}^{+\infty} \Psi(x) dx = 1$

(52) is a linear differential equation with a **variable coefficient**

solution can be expressed through **special functions** (in next semester course)

main result eigenvalues have the form ☛ $\varepsilon_j = \left(j + \frac{1}{2} \right) \hbar\omega \quad j = 0, 1, 2, \cdots$ (53)

$\omega = \sqrt{k/m}$ ☛ frequency of oscillations

energies are equally spaced and states are non-degenerate ☛ $g_j = 1 \quad \forall j$

ground state $\varepsilon_0 = \hbar\omega/2$ is not zero as would be case for a classical oscillator

This quantum ground-state energy is called zero-point energy

PARTITION FUNCTION

$$Z = \sum_{j=0}^{\infty} g_j e^{-\beta \varepsilon_j} = e^{-\beta \hbar\omega/2} \sum_{j=0}^{\infty} e^{-\beta\hbar\omega j} \qquad (54)$$

$$= e^{\beta\hbar\omega/2}(1 + e^{-\beta\hbar\omega} + e^{-2\beta\hbar\omega} + \cdots)$$

using result for geometrical progression ↴

$$1 + x + x^2 + x^3 + \ldots = (1 - x)^{-1} \qquad x < 1$$

☟

$$Z = \frac{e^{-\beta\hbar\omega/2}}{1 - e^{-\beta\hbar\omega}} = \frac{e^{\theta/(2T)}}{1 - e^{-\theta/T}} \qquad (55)$$

characteristic temperature ☛ $\theta = \hbar\omega/k$

OCCUPATION NUMBERS

$$\frac{N_j}{N} = \frac{e^{-\varepsilon_j/kT}}{Z} = e^{-\varepsilon_j/kT}[e^{\theta/2T}(1-e^{-\theta/T})]$$
$$= (1-e^{-\theta/T})e^{-\varepsilon_j/kT+\theta/2T}$$

using ☛ $$-\frac{\varepsilon_j}{kT} + \frac{\theta}{2T} = -\left(j+\frac{1}{2}\right)\frac{\hbar\omega}{kT} + \frac{\hbar\omega}{2kT} = -j\frac{\hbar\omega}{kT} = -j\frac{\theta}{T}$$

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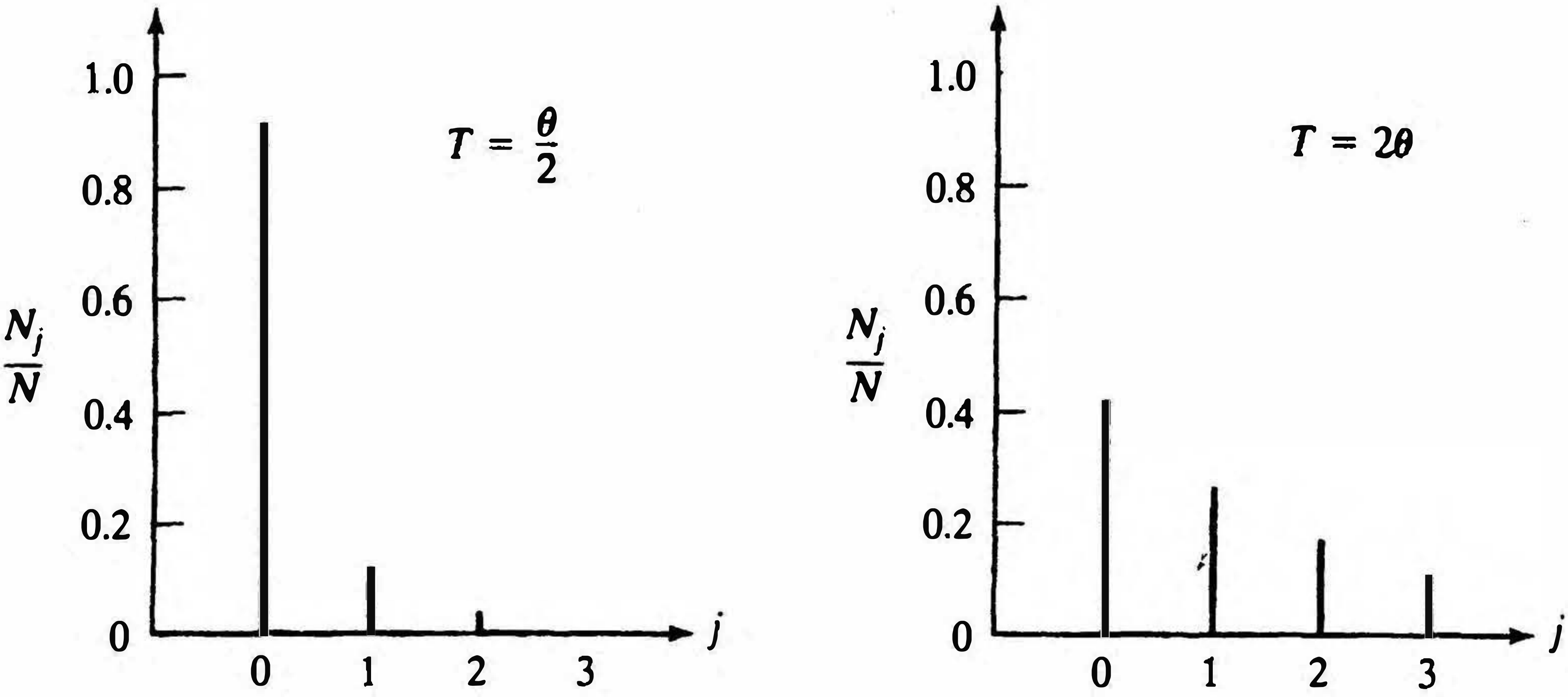
$$\frac{N_j}{N} = e^{-j\theta/T}(1-e^{-\theta/T}) \qquad (56)$$

EXAMPLE

Fractional occupation numbers for quantized linear oscillators



the lower the temperature the more rapidly occupation numbers decrease with j

U

Internal (average) energy of ensemble of oscillators is

$$U = -N\left(\frac{\partial \ln Z}{\ln \beta}\right)_V = NkT^2\left(\frac{\partial \ln Z}{\partial T}\right)_V = Nk\theta\left(\frac{1}{2} + \frac{1}{e^{\theta/T}-1}\right) \quad (57)$$

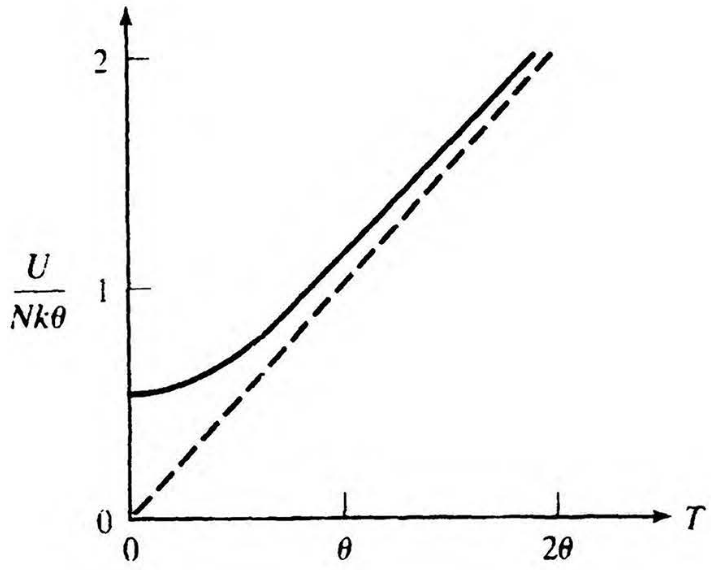
The limiting low- and high-temperature cases of this expression are

$$U \simeq \begin{cases} N\hbar\omega/2 & \text{if } kT \ll \hbar\omega \\ NkT & \text{if } kT \gg \hbar\omega \end{cases} \quad (58)$$

This is what we would expect from a diatomic molecule

with two vibrational degrees of freedom

(kinetic and potential energy)



☛ $$\lim_{T\to 0} U = N\hbar\omega/2 \quad (59)$$

HEAT CAPACITY OF HARMONIC OSCILLATORS

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = Nk\theta \frac{\partial}{\partial T}(e^{\theta/T} - 1)^{-1}$$

$$= Nk \left(\frac{\theta}{T}\right)^2 \frac{e^{\theta/T}}{(e^{\theta/T} - 1)^2}$$

@ high temperatures ☛ $\theta/T \ll 1$

$$C_V = Nk \left(\frac{\theta}{T}\right)\left(\frac{\theta}{T}\right)^{-2} = Nk$$

heat capacity approaches a constant

@ low temperatures ☛ $\theta/T \gg 1 \ \Rightarrow e^{\theta/T} \gg 1$

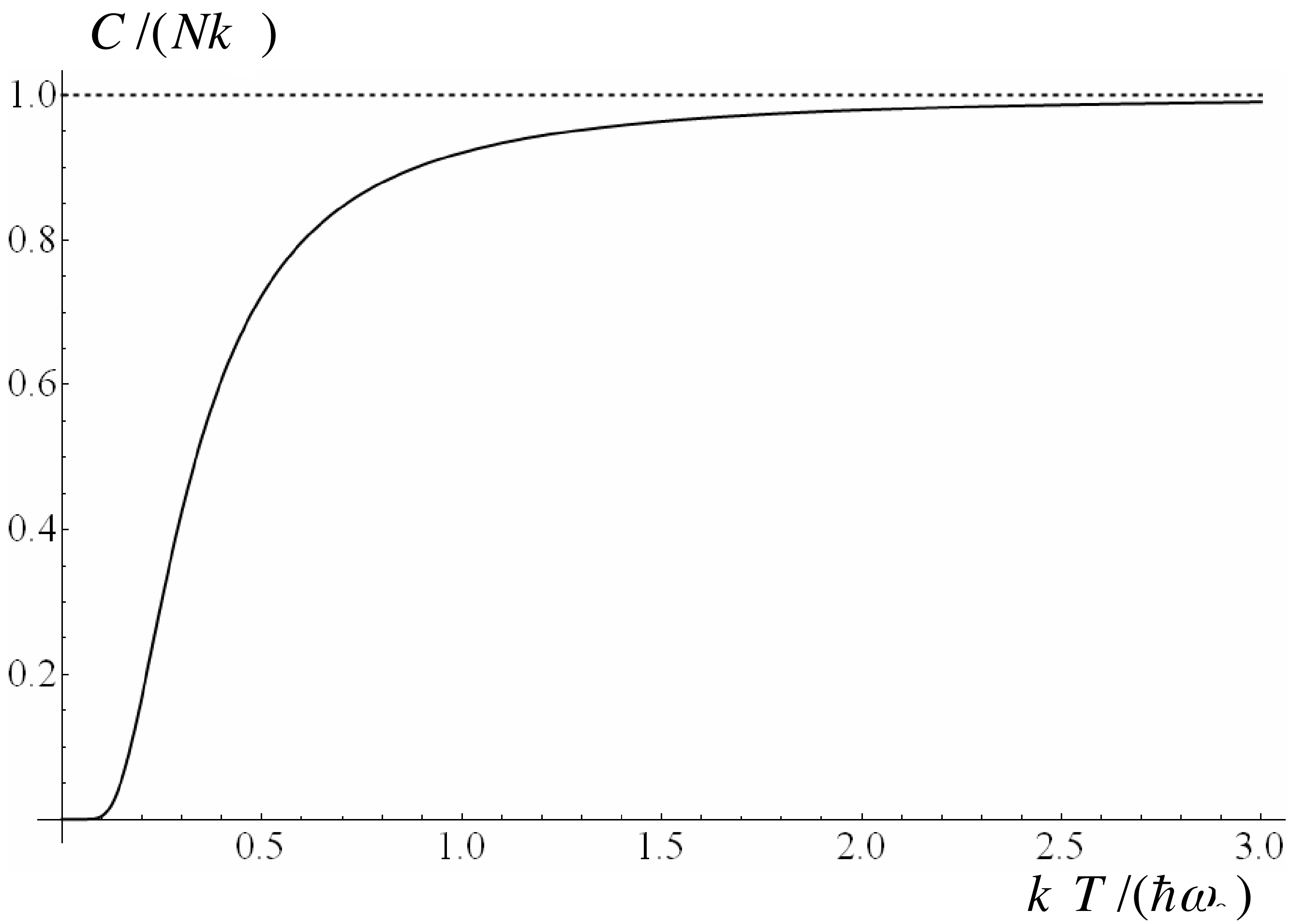
$$\frac{e^{\theta/T}}{(e^{\theta/T} - 1)^2} \to e^{-\theta/T} \Rightarrow C_V \to Nk \left(\frac{\theta}{T}\right)^2 e^{-\theta/T}$$

Rate at which exponential factor approaches zero as $T \to 0$

is greater than rate of growth of $(\theta/T)^2$ ↴

$$\lim_{T \to 0} C_V = 0$$

VARIATION WITH TEMPERATURE OF HEAT CAPACITY



VIBRATIONAL MODES OF DIATOMIC MOLECULES

Average quantum number of oscillator ☛ $n \equiv \langle j \rangle = \frac{1}{Z} \sum_{j=0}^{\infty} j e^{-\beta \varepsilon_j}$ (60)

$$n = \frac{1}{Z} \sum_{j=0}^{\infty} \left(\frac{1}{2} + j \right) e^{-\beta\varepsilon_j} - \frac{1}{Z} \sum_{j=0}^{\infty} \frac{1}{2} e^{-\beta \varepsilon_j} = \frac{1}{\hbar\omega} \frac{1}{Z} \sum_{j=0}^{\infty} \varepsilon_j e^{-\beta\varepsilon_j} - \frac{Z}{2Z}$$

$$= -\frac{1}{\hbar\omega} \frac{1}{Z} \frac{\partial Z}{\partial \beta} - \frac{1}{2} = \frac{U}{N\hbar\omega} - \frac{1}{2}$$

Using (57) ☛ $n = \frac{1}{e^{\beta\hbar\omega} - 1}$ and $U = N\hbar\omega \left(\frac{1}{2} + n \right)$ (61)

At low temperatures $kT \ll \hbar\omega$ ☛ n becomes exponentially small

This means that oscillator is predominantly in its ground state $j = 0$

Vibrational degrees of freedom are getting frozen out at low temperatures

CLASSICAL LIMIT

At high temperatures $kT \gg \hbar\omega$ ☛ $n \simeq \dfrac{kT}{\hbar\omega}$

At high temperatures many levels are populated

distribution function $e^{-\beta\varepsilon_\nu}$ only slightly changes from one level to other

relative change ☛ $\dfrac{e^{-\beta\varepsilon_j} - e^{-\beta\varepsilon_{j+1}}}{e^{-\beta\varepsilon_j}} = 1 - e^{-\beta(\varepsilon_{j+1}-\varepsilon_j)} = 1 - e^{-\beta\hbar\omega}$

$$\simeq 1 - 1 + \beta\hbar\omega = \frac{\hbar\omega}{kT} \ll 1$$

Homework ☛ it is straightforward to show $\rho(\varepsilon) = (\hbar\omega)^{-1}$

summation in (54) can be replaced by integration

$$Z = \int_0^\infty d\varepsilon \; \rho(\varepsilon) \; e^{-\beta\varepsilon} = \frac{1}{\hbar\omega\beta} = \frac{kT}{\hbar\omega}$$

$$U = -N\frac{\partial \ln Z}{\partial\beta} = -N\frac{\partial \ln \frac{1}{\beta} + \cdots}{\partial\beta} = N\frac{\partial \ln \beta + \cdots}{\partial\beta} = \frac{N}{\beta} = NkT$$

QUANTUM MECHANICS INTERLUDE

Angular Momentum

Classically, angular momentum with respect to the origin is given by the formula:

$$\vec{\mathrm{L}} = \vec{\mathrm{r}} \times \vec{\mathrm{p}} \tag{1}$$

In Cartesian coordinates, the components are

$$L_x = yp_z - zp_y; \quad L_y = zp_x - xp_z; \quad L_z = xp_y - yp_x \,. \tag{2}$$

The corresponding quantum mechanical operators are obtained using $\vec{\mathrm{p}} \to (\hbar/i)\nabla$:

$$L_x = \frac{\hbar}{i}\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right) \tag{3}$$

$$L_y = \frac{\hbar}{i}\left(y\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right) \tag{4}$$

$$L_z = \frac{\hbar}{i}\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right) \tag{5}$$

The components of $\vec{\mathrm{L}}$ do not commute. By explicit calculation:

$$[L_x, L_y] = i\hbar L_z; \quad [L_y, L_z] = i\hbar L_x; \quad [L_z, L_x] = i\hbar L_y \,. \tag{6}$$

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QUANTUM MECHANICS INTERLUDE II

Angular Momentum Eigenstates

As the components do not commute, the generalized uncertainty principle tells us that:

$$\sigma_{L_x}\sigma_{L_y} \geq \frac{\hbar}{2}|\langle L_z\rangle| \tag{7}$$

Perhaps surprisingly, the *square* of the *total* angular momentum

$$L^2 \equiv L_x^2 + L_y^2 + L_z^2 \tag{8}$$

does commute with each of the components:

$$[L^2, L_x] = [L^2, L_y] = [L^2, L_z] = 0\,. \tag{9}$$

This means that (with luck) we can find simultaneous eigenstates of L^2 and one of the components, L_z for example:

$$L^2 f = \lambda f; \qquad L_z f = \mu f\,. \tag{10}$$

QUANTUM MECHANICS INTERLUDE III

Angular Momentum Ladder Operators

We can use a ladder operator technique to determine the eigenvalues of L^2 and L_z algebraically.

$$L_\pm = L_x \pm iL_y \tag{11}$$

With the definition of the ladder operators we calculate the commutators of the ladder operators with L^2 and L_z:

$$[L_z, L_\pm] = \pm\hbar L_\pm; \quad [L^2, L_\pm] = 0\,. \tag{12}$$

If f is an eigenfunction of *both* L^2 and L_z, then $L_\pm f$ also is:

$$L^2(L_\pm f) = L_\pm(L^2 f) = L_\pm(\lambda f) = \lambda(L_\pm f)\,; \tag{13}$$

$$\begin{aligned} L_z(L_\pm f) &= (L_z L_\pm - L_\pm L_z)f + L_\pm L_z f && (14) \\ &= \pm\hbar L_\pm f + L_\pm(\mu f) = (\mu \pm \hbar)(L_\pm f) && (15) \end{aligned}$$

QUANTUM MECHANICS INTERLUDE IV

The Angular Momentum Ladder

The ladder operators $L_\pm$ raise and lower the eigenvalues of L_z by $\hbar$ while leaving the eigenvalues of L^2 unchanged. For each value of λ we have a ladder of states with values of μ separated by $\hbar$. If f is simultaneously an eigenfunction of L^2 and of $L_\pm$, then $\mu \leq \lambda$

We designate the state with the largest value of μ as the *top* of the ladder and denote it f_t and write its eigenvalues:

$$L_z f_t = \hbar \ell f_t; \quad L^2 f_t = \lambda f_t\,. \tag{16}$$

Note that we have introduced ℓ as the *maximum eigenvalue* of L_z With a bit of manipulation, we can calculate λ in terms of ℓ.

$$\begin{aligned} L_\pm L_\mp &= (L_x \pm i L_y)(L_x \mp i L_x) && (17) \\ &= L_x^2 + L_y^2 \mp i((L_x L_y - L_y L_x) \;=\; L^2 - L_z^2 \mp i(i\hbar L_z) && (18) \end{aligned}$$

$$L^2 = L_\pm L_\mp + L_z^2 \mp \hbar L_z \tag{19}$$

$$L^2 f_t \;=\; (L_- L_+ + L^2 + \hbar L_z) f_t \;=\; (0 + \hbar^2 \ell^2 + \hbar^2 \ell) f_t \tag{20}$$

$$\lambda \;=\; \hbar^2 \ell(\ell + 1) \tag{21}$$

QUANTUM MECHANICS INTERLUDE V

Angular Momentum Eigenvalues

Operating from the bottom of the ladder $L_z f_b = \hbar \bar{\ell} f_b$, we find

$$\lambda = \hbar^2 \bar{\ell}(\bar{\ell} - 1) \tag{22}$$

from which we conclude that

$$\bar{\ell} = -\ell \tag{23}$$

L_z has eigenvalues $m\hbar$ where m varies from $-\ell$ to ℓ in integer steps. Denoting the number of steps N,

$$\ell = -\ell + N \tag{24}$$

$$2\ell = N \tag{25}$$

$$\ell = N/2 \tag{26}$$

This implies that ℓ is either integer or half-integer. The eigenfunctions are characterized by the quantum numbers ℓ and m:

$$L^2 f_\ell^m = \hbar^2 \ell(\ell + 1) f_\ell^m; \quad L_z f_\ell^m = \hbar m f_\ell^m \tag{27}$$

$$m = -\ell, -\ell + 1, \cdots, \ell - 1, \ell \tag{28}$$

SPECTRUM OF ROTATIONAL STATES

Rotation of diatomic molecule
is modeled as motion of quantum mechanical rigid rotator

Rotation take place about axis through center of mass of molecule
and perpendicular to line joining two atoms

moment of inertia ☛ $I = \mu r_0^2$ reduced mass ☛ $\mu = m_1 m_2/(m_1 + m_2)$

Solution of stationary Schrödinger equation yields

$$\hat{\mathbf{L}}^2 f_l^m = \hbar^2 l(l+1) f_l^m, \qquad l = 0, 1, 2, \cdots$$

$$\hat{L}_3 f_l^m = \hbar m, \qquad m = -l, -l+1, \cdots, l-1, l$$

energy levels of linear rigid rotator with two degrees of freedom

$$\varepsilon_l = l(l+1)\frac{\hbar^2}{2I}$$

principal moments of inertia ☛ $(I, I, 0)$

ROTATIONAL PARTITION FUNCTION OF THE MOLECULE

For diatomic molecules there are $2l+1$ degenerate levels

For fully symmetric body ☛ $I_1 = I_2 = I_3 = I$

degeneracy of quantum level l ☛ $g_l = (2l+1)^2$

Rotational partition function for symmetric body and for a diatomic molecule

☟

$$Z = \sum_l g_l e^{-\beta\varepsilon_l} \qquad g_l = (2l+1)^\xi \qquad \xi = \begin{cases} 2 & \text{symmetric body} \\ 1 & \text{diatomic molecule} \end{cases} \tag{62}$$

Z cannot be calculated analytically

LOW-TEMPERATURE LIMIT

In low-temperature limit ☛ most of rotators are in their ground state $l = 0$
and very few are in first excited state $l = 1$

Discarding all other values of l

$$Z \cong 1 + 3^{\xi} \exp\left(-\frac{\beta\hbar^2}{I}\right)$$

Rotational internal energy

$$U = -N\frac{\partial \ln Z}{\partial\beta} = 3^{\xi}\frac{\hbar^2}{I}\exp\left(-\frac{\beta\hbar^2}{I}\right) = 3^{\xi}\frac{\hbar^2}{I}\exp\left(-\frac{\hbar^2}{Ik_BT}\right)$$

is exponentially small

Heat capacity

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = 3^{\xi}k_B\left(\frac{\hbar^2}{Ik_BT}\right)^2\exp\left(-\frac{\hbar^2}{Ik_BT}\right)$$

is also exponentially small

HIGH-TEMPERATURE LIMIT

In high-temperature limit ☛ $T \gg \dfrac{\hbar^2}{2Ik}$

many energy levels are thermally populated ☛ replace summation by integration in (62)

using ↴

$$g_l \cong (2l)^\xi \qquad \varepsilon_l \equiv \varepsilon \cong \frac{\hbar^2 l^2}{2I} \qquad \frac{\partial \varepsilon}{\partial l} = \frac{\hbar^2 l}{I} \qquad \frac{\partial l}{\partial \varepsilon} = \frac{I}{\hbar^2}\sqrt{\frac{\hbar^2}{2I\varepsilon}} = \sqrt{\frac{I}{2\hbar^2\varepsilon}}$$

☟

$$Z \cong \int_0^\infty dl\, g_l e^{-\beta\varepsilon_l} \cong 2^\xi \int_0^\infty dl\, l^\xi e^{-\beta\varepsilon_l} = 2^\xi \int_0^\infty d\varepsilon \frac{\partial l}{\partial \varepsilon} l^\xi e^{-\beta\varepsilon}$$

☟

$$Z \cong 2^\xi \sqrt{\frac{I}{2\hbar^2}} \int_0^\infty d\varepsilon \frac{1}{\sqrt{\varepsilon}} \left(\frac{2I\varepsilon}{\hbar^2}\right)^{\xi/2} e^{-\beta\varepsilon} = 2^{(3\xi-1)/2} \left(\frac{I}{\hbar^2}\right)^{(\xi+1)/2} \int_0^\infty d\varepsilon\, \varepsilon^{(\xi-1)/2}\, e^{-\beta\varepsilon}$$

$$= 2^{(3\xi-1)/2} \left(\frac{I}{\beta\hbar^2}\right)^{(\xi+1)/2} \int_0^\infty dx\, x^{(\xi-1)/2}\, e^{-x} \propto \beta^{-(\xi+1)/2}$$

For $\xi = 1$ ☛ $Z = \dfrac{2I}{\hbar^2\beta}$

INTERNAL ENERGY AND HEAT CAPACITY

$$U = -N\frac{\partial \ln Z}{\partial \beta} = \frac{\xi+1}{2}N\frac{\partial \ln \beta}{\partial \beta} = \frac{\xi+1}{2}N\frac{1}{\beta} = \frac{\xi+1}{2}Nk_BT \quad (63)$$

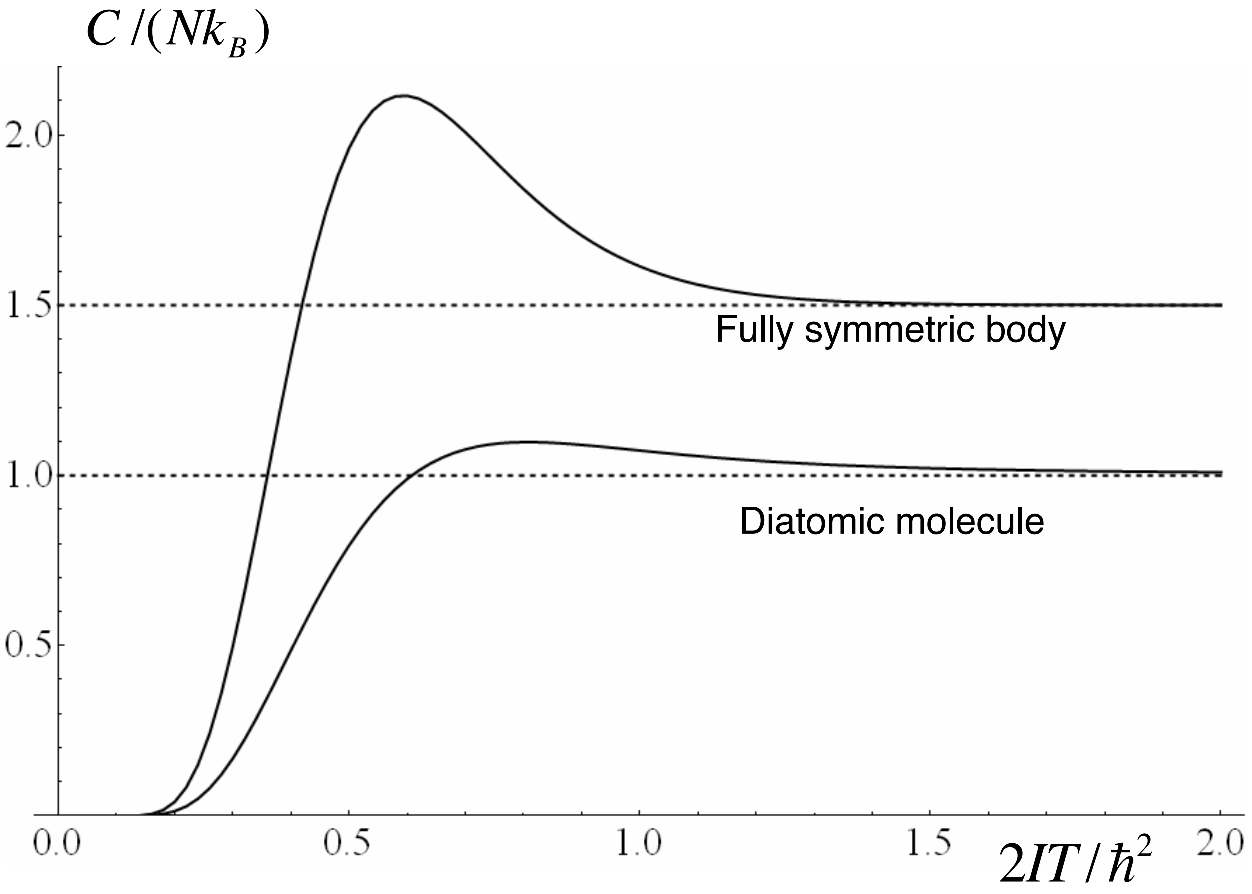
$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = \frac{\xi+1}{2}Nk_B$$

$f = \xi + 1$ ☛ number of degrees of freedom

$f = 2$ for diatomic molecule and $f = 3$ for fully symmetric rotator

This result confirms principle of equipartition of energy over degrees of freedom in classical limit which requires high enough temperatures

ROTATIONAL HEAT CAPACITY



CLASSICAL PARTITION FUNCTION AT HIGH-T

General case of all moments of inertia different ☛ $E_{\rm rot} = \frac{L_1^2}{2I_1} + \frac{L_2^2}{2I_2} + \frac{L_3^2}{2I_3}$

Dynamical variables here are angular momentum components L_1, L_2 and L_3

partition function can be obtained by integration with respect to them

$$\begin{aligned} Z_{\rm class} &= \int_{-\infty}^{\infty} dL_1\, dL_2\, dL_3 \exp\left(-\beta E_{\rm rot}\right) \\ &= \int_{-\infty}^{\infty} dL_1 \exp\left(-\frac{\beta L_1^2}{2I_1}\right) \times \int_{-\infty}^{\infty} dL_2 \exp\left(-\frac{\beta L_2^2}{2I_2}\right) \times \int_{-\infty}^{\infty} dL_3 \exp\left(-\frac{\beta L_3^2}{2I_3}\right) \\ &= \sqrt{\frac{2I_1}{\beta} \times \frac{2I_2}{\beta} \times \frac{2I_3}{\beta}} \left(\int_{-\infty}^{\infty} dx\, e^{-x^2}\right)^3 \propto \beta^{-3/2} \end{aligned}$$

$Z_{\rm class}$ contains some additional coefficients

e.g. ☛ from integration over orientations of molecule

These coefficients are irrelevant in calculation of internal energy

$$U = -N \frac{\partial \ln Z}{\partial \beta} = \frac{3}{2} N \frac{\partial \ln \beta}{\partial \beta} = \frac{3}{2} N k_B T \qquad (64)$$

that coincides with (63) for $\xi = 2$

CLASSICAL PARTITION FUNCTION AT HIGH-T II

For diatomic molecule ☛ $E_{\rm rot} = \frac{L_1^2}{2I_1} + \frac{L_2^2}{2I_2}$

partition function becomes ↴

$$Z_{\rm class} = \int_{-\infty}^{\infty} dL_1\, dL_2 \exp\left(-\beta E_{\rm rot}\right)$$

$$= \int_{-\infty}^{\infty} dL_1 \exp\left(-\frac{\beta L_1^2}{2I_1}\right) \times \int_{-\infty}^{\infty} dL_2 \exp\left(-\frac{\beta L_2^2}{2I_2}\right)$$

$$= \sqrt{\frac{2I_1}{\beta} \times \frac{2I_2}{\beta}} \left(\int_{-\infty}^{\infty} dx\, e^{-x^2}\right)^2 \propto \beta^{-1}$$

This leads to ↴

$U = N k_B T$ ☛ in accordance with (63) for $\xi = 1$