CHM 421/621 Statistical Mechanics

Lecture 27 Non-degenerate systems

Ensembles

Lecture Plan

Ideal gas revisited : Quantum particles in a 3-d box

Classical equipartition theorem

Quantum haromonic oscillator

Non-degenerate Systems

Ideal gas revisited: Quantum particles in a 3-d box

Gas is at constant temperature *T* and constant volume $V = L^3$

Allowed energies for 1 particle

$$\epsilon(\vec{k}) = \frac{\hbar^2 k^2}{2m} \qquad k_\alpha = \frac{\pi n_\alpha}{L} \quad (\alpha = x, y, z)$$

$$n_\alpha = 1, 2, \ldots$$

Number of states with energy less than ϵ

$$N(\epsilon) = \frac{1}{8} \times \frac{4}{3}\pi \left(\frac{2m\epsilon}{\hbar^2}\right)^{\frac{3}{2}} \times \frac{L^3}{\pi^3} = \frac{4}{3\sqrt{\pi}} \left(\frac{\sqrt{2\pi m\epsilon}}{h}\right)^3 V$$

Therefore

$$N(k_B T) = \frac{4}{3\sqrt{\pi}} \frac{V}{\Lambda^3} \approx 0.75 \frac{V}{\Lambda^3}$$

Non-degenerate Systems

Ideal gas revisited: Quantum particles in a 3-d box

Gas is at constant temperature T and constant volume $V=L^3$

To use the Boltzmann approximation for the particles we must have

$$N(k_BT) >> N$$

$$\frac{V}{\Lambda^3} >> N \qquad \Longrightarrow \qquad \boxed{\Lambda^3 << \frac{V}{N}}$$

i.e. the average inter particle separation should be much larger than the thermal de Broglie wavelength.

This can happen for dilute gases and at high temperatures.

$$Z \approx \frac{z^N}{N!}$$

Non-degenerate Systems

Ideal gas revisited: Quantum particles in a 3-d box

Gas is at constant temperature *T* and constant volume $V=L^3$

Consider that such a condition is met we can write

$$Z \approx \frac{z^N}{N!}$$

$$z = \frac{V}{\pi^3} \int_0^\infty dk_x \int_0^\infty dk_y \int_0^\infty dk_z \, \exp\left(-\beta \frac{\hbar^2 k^2}{2m}\right)$$

$$= \frac{V}{\pi^3} \left(\int_0^\infty dk_x \, \exp\left(-\beta \frac{\hbar^2 k_x^2}{2m}\right) \right)^3$$

$$= \frac{V}{8\pi^3} \left(\frac{2\pi m k_B T}{\hbar^2} \right)^{\frac{3}{2}} = \frac{V}{\Lambda^3}$$

$$\Rightarrow \quad Z = \frac{1}{N!} \left(\frac{V}{\Lambda^3} \right)^N$$

Non-degenerate systems

Classical equipartition theorem

Consider a classical system with energy that be written as

$$E(s_1, s_2, s_3, \ldots, s_M, s_{M+1}, \ldots,) = \sum_{k=1}^{M} c_k s_k^2 + f(s_{M+1}, s_{M+2}, \ldots)$$

i.e. with *M* variables appearing through a quadratic dependence.

The classical partition function can then be written as

$$Z(N,V,T) = \int ds_1 \int ds_2 \cdots \int ds_M \cdots \exp(-\beta \sum_{k=1}^{M} c_k s_k^2) \times \exp(-\beta f(s_{M+1}, s_{M+2}, \ldots))$$

$$= \prod_{k=1}^{M} \left(\int ds_k \, \exp(-\beta c_k s_k^2) \right) \times Z_{rest}$$

where $Z_{rest} = \int ds_{M+1} \int ds_{M+2} \cdots \exp\left(-\beta f(s_{M+1}, s_{M+2}, \ldots)\right)$

Non-degenerate Systems

Classical equipartition theorem

$$Z(N,V,T) = \prod_{k=1}^{M} \left(\frac{\pi}{\beta c_k} \right)^{\frac{1}{2}} \times Z_{rest}$$

$$\overline{E} = -\frac{d \ln Z}{d\beta}$$

$$= \frac{M}{2} k_B T + \overline{E}_{rest}$$

i.e every quadratic term in the energy of a classical system contributes 1/2 $k_B T$ to the average energy at a given temperature *T*.

This is the classical equipartition theorem. One expects that each such term would also contribute 1/2 k_B to the specific heat at constant volume.

Non-degenerate Systems

Classical equipartition theorem

E.g. Monatomic ideal gas

$$E = \sum_{i=1}^{N} \frac{1}{2m} \left(p_{i,x}^2 + p_{i,y}^2 + p_{i,z}^2 \right)$$

$$\overline{E} = \frac{3}{2} N k_B T \qquad C_V = \frac{3}{2} N k_B$$

Answer comes out to be same for the quantum version in the non-degenerate limit.
(Why??)

Non-degenerate Systems

Classical equipartition theorem

E.g. Harmonic oscillator

$$E = \sum_{i=1}^{N} \left(\frac{p_i^2}{2m} + \frac{1}{2} m \omega^2 x_i^2 \right)$$

$$\overline{E} = N k_B T \qquad C_V = N k_B$$

Non-degenerate Systems

Classical Rigid Rotor

Two masses separated by a fixed distance *R*

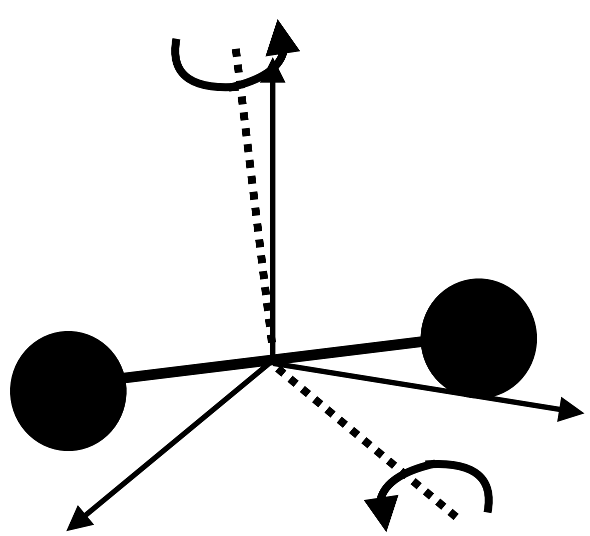
Classical version

$$E = \sum_{j=1,N} \frac{1}{2} I \left(\omega_{j,1}^2 + \omega_{j,2}^2\right)$$

Assuming centre of mass frame

$\omega_{j,\mu}$ Angular velocity of *j*th rotor about axis μ

$I = \mu R^2$ Moment of inertia



Average energy and specific heat per particle

$$\bar{\epsilon} = k_B T \qquad c_V = k_B$$

Non-degenerate Systems

Ideal diatomic gas

$$E_{diatomic} = E_{trans} + E_{rot} + E_{vib}$$

$$\implies z_{diatomic} = z_{trans} \times z_{rot} \times z_{vib}$$

$$\implies \bar{\epsilon}_{diatomic} = \epsilon_{trans} + \epsilon_{rot} + \epsilon_{vib}$$

$$\implies c_{V\,diatomic} = c_{V\,trans} + c_{V\,rot} + c_{V\,vib}$$

For the quantum case there will be addition terms as we shall see

Non-degenerate Systems

Quantum Harmonic Oscillator

$$\hat{H} = \frac{\hat{p}^2}{2m} + \frac{1}{2}m\omega^2\hat{x}^2$$

$$E_n = (n + \frac{1}{2})\hbar\omega \qquad n=0,1,2,\ldots$$

Non-degenerate case

$$z = \exp(-\beta\frac{\hbar\omega}{2})\sum_{n=0}^{\infty}\exp(-\beta n\hbar\omega)$$

$$= \frac{\exp(-\beta\frac{\hbar\omega}{2})}{1 - \exp(-\beta\hbar\omega)}$$

Non-degenerate Systems

Quantum Harmonic Oscillator

$$\bar{\epsilon} = \overline{E}/N = -\frac{\partial \ln z}{\partial \beta}$$
$$= \frac{\hbar\omega}{2} + \frac{\hbar\omega}{e^{\frac{\hbar\omega}{k_B T}} - 1}$$

For typical diatomic vibration frequencies at room temperature we have $\frac{\hbar\omega}{k_B T} << 1$

So energy per oscillator is

$$\bar{\epsilon} - \epsilon_0 \approx k_B T$$

Similarly as T -> 0

$$\bar{\epsilon} - \epsilon_0 \approx k_B \Theta_{vib}\ e^{\Theta_{vib}/T}$$

In general classical result applies when $T >> \Theta_{vib}$

$$\Theta_{vib} \equiv \frac{\hbar\omega}{k_B}$$

Non-degenerate Systems

Quantum Harmonic Oscillator

Fraction of excited molecules

$$f_n = \frac{e^{-\beta(n+\frac{1}{2})\hbar\omega}}{z(T)}$$

$$f_{n>0} = 1 - f_0 = 1 - \frac{e^{-\frac{\beta}{2}\hbar\omega}}{z(T)}$$

$$= e^{-\frac{\Theta_{vib}}{T}}$$

	$\Theta_{vib}(K)$
H_2	6215
HCl	4227
Cl_2	810
I_2	310

Weaker the bond more thermally excited the molecule.

Non-degenerate Systems

Quantum Rigid Rotor

$$\hat{H}_{rot} = \frac{\hbar^2}{2I}\hat{L}^2$$ For each rotor

Eigenvalues

$$E_J = J(J+1)\frac{\hbar^2}{2I} \qquad J = 0, 1, 2, \ldots$$

These states are *2J+1* degenerate
(since M_J = *-J,-J+1,…,J* and energy doesn't depend on M_J)

$$B = \frac{\hbar^2}{2I}$$ Rotational constant in energy units

Typical values

	I X 10^{47} (kg-m^3)	B/k_B (K)
H_2	0.461	87.6
HF	1.34	30.1
HCl	2.65	15.2
I_2	745.0	0.054

Non-degenerate Systems

Quantum Rigid Rotor

Partition function (non-degenerate case)

$$\Delta E = 2(J+1)B \sim B$$ For small *J*

$$\implies T/\Theta_r >> 1$$

For most diatomic gases at room temperature

$$\Theta_r \equiv B/k_B$$ Characteristic rotation temperature

$$z_{rot} = \sum_{J=0}^{\infty} (2J+1)\ \exp(-\beta J(J+1)B)$$

$$= \sum_{J=0}^{\infty} (2J+1)\ \exp\left(-J(J+1)\frac{\Theta_r}{T}\right)$$

$$\approx \int_0^{\infty} d(J(J+1)) \exp\left(-J(J+1)\frac{\Theta_r}{T}\right) = \frac{T}{\Theta_r}$$

Non-degenerate Systems

Quantum Rigid Rotor

Partition function (non-degenerate case)

For the general case we can use the following

$$\sum_{n=a}^{b} f(n) \approx \int_a^b f(n)\ dn \ + \ \frac{1}{2}\left[f(b) + f(a)\right]$$

Euler-Maclaurin series

$$+\sum_{k=1}^{\infty}(-1)^k \frac{B_{2k}}{(2k)!}\left(f^{(2k-1)}(b) - f^{(2k-1)}(a)\right)$$

$$a = 0 \quad b = \infty \quad n = J$$

$$f(\infty) = f'(\infty) = \cdots = 0$$

$$z_{rot} = \frac{T}{\Theta_r} + \frac{1}{3} + \frac{1}{15}\frac{\Theta_r}{T} + \frac{4}{315}\left(\frac{\Theta_r}{T}\right)^2 + O\left(\left(\frac{\Theta_r}{T}\right)^3\right)$$

Provided that $\frac{\Theta_r}{T} < 1$

Non-degenerate Systems

Quantum Rigid Rotor

Energy and specific heat

For $T/\Theta_r >> 1$ we recover the classical result

Average energy and specific heat per particle

$$\bar{\epsilon} = k_B T \qquad c_V = k_B$$