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5.62 Physical Chemistry II
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5.62 Lecture #10: Quantum vs. Classical. q_{trans} . **Equipartition. Internal Degrees of Freedom.**

GOAL: Calculate average translational energy via quantum and classical descriptions and compare results.

QUANTUM DESCRIPTION — Calculate $\bar{\epsilon}_x$ — average kinetic energy in x-direction

$$\begin{aligned}\bar{\epsilon}_x &= \int_0^{\infty} \epsilon_x P(\epsilon_x) d\epsilon_x \\ P(\epsilon_x) &= (\pi kT)^{-1/2} \epsilon_x^{-1/2} e^{-\epsilon_x/kT} \\ \bar{\epsilon}_x &= \left(\frac{1}{\pi kT}\right)^{1/2} \int_0^{\infty} \epsilon_x^{1/2} e^{-\epsilon_x/kT} d\epsilon_x \\ \bar{\epsilon}_x &= \left(\frac{1}{\pi kT}\right)^{1/2} \frac{kT}{2} (\pi kT)^{1/2} = \frac{1}{2} kT\end{aligned}$$

This is not an accident. It is our first glimpse of “equipartition” of energy, $\frac{1}{2}kT$ into each independent degree of freedom.

Integral table for two useful integrals

$$\begin{aligned}\int_0^{\infty} x^{1/2} e^{-ax} dx &= \frac{\pi^{1/2}}{2a^{3/2}} && \text{(dimension: length}^{3/2}\text{)} \\ \int_0^{\infty} x^{-1/2} e^{-ax} dx &= (\pi/a)^{1/2} && \text{(dimension: length}^{1/2}\text{)}\end{aligned}$$

Since the translational energies in each dimension are uncorrelated, average total energy is the sum of the average energy in each direction. Also, as a consequence of the separability of the Hamiltonian with respect to x, y, z coordinates, total E is sum of $E_x + E_y + E_z$.

$$\bar{E} = \bar{\epsilon}_x + \bar{\epsilon}_y + \bar{\epsilon}_z$$

$$\frac{1}{2}kT + \frac{1}{2}kT + \frac{1}{2}kT = \frac{3}{2}kT$$

Each degree of freedom contributes $\frac{1}{2}kT$ to total energy.

Agrees with result from ensemble average

$$\bar{\epsilon} = \bar{E} = kT^2 \left(\frac{\partial \ln Q_{\text{trans}}}{\partial T} \right)_{N,V} = \sum_{\alpha} P_{\alpha} E_{\alpha} = \frac{3}{2} kT$$

CLASSICAL MECHANICAL DESCRIPTION — calculate $\bar{\epsilon}$

State of a molecule is described by $\tilde{\mathbf{p}}$ momentum, $\tilde{\mathbf{q}}$ position. The energy of N-molecule system is $\epsilon(\tilde{\mathbf{p}}^{3N}, \tilde{\mathbf{q}}^{3N})$, which is a continuous function of 6N variables.

$$\begin{aligned}
 q_{\text{trans}} &= \sum_i e^{-\epsilon_i/kT} && \text{let's assume this by analogy} && \int \dots \int e^{-\epsilon(\tilde{\mathbf{p}}, \tilde{\mathbf{q}})/kT} d\tilde{\mathbf{p}} d\tilde{\mathbf{q}} \\
 &\text{quantum} && \Rightarrow && \text{classical — integral over 3} \\
 &&& && \text{momentum and 3 position} \\
 &&& && \text{coordinates for each particle} \\
 &&& && \downarrow = p_x^2 + p_y^2 + p_z^2 \\
 q_{\text{trans,cl}} &= \iiint d\tilde{\mathbf{q}} \iiint d\tilde{\mathbf{p}} e^{-\epsilon(\tilde{\mathbf{p}}, \tilde{\mathbf{q}})/kT} \\
 &= V \int dp_x e^{-p_x^2/2mkT} \int dp_y e^{-p_y^2/2mkT} \int dp_z e^{-p_z^2/2mkT} \\
 &= V \left[\int_{-\infty}^{\infty} dp_x e^{-p_x^2/2mkT} \right]^3 = V (2\pi mkT)^{3/2}
 \end{aligned}$$

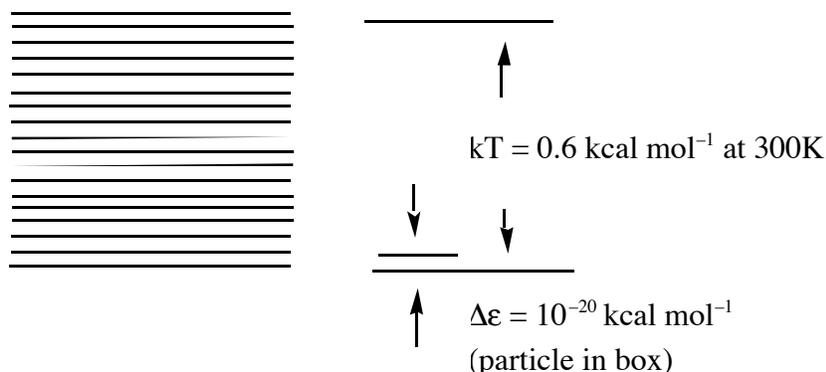
[$q_{\text{trans,cl}}$ should be dimensionless, but this has units $m^3 l^6 t^{-3} = h^3$]

The need to divide by a factor of h^3 was recognized by Boltzmann even before Planck “invented” h . It is impossible for a trajectory in phase space to intersect itself. [Why? Because the classical Hamiltonian is a function of \mathbf{q}, \mathbf{p} . If the system is at $\mathbf{q}(t_1), \mathbf{p}(t_1)$ at t_1 then the \mathbf{H} tells us the values of \mathbf{q} and \mathbf{p} at $t_1 + \delta t$. If the system returns to $\mathbf{q}(t_1), \mathbf{p}(t_1)$ at t_2 , then it must move to $\mathbf{q}(t_1 + \delta t), \mathbf{p}(t_1 + \delta t)$ at $t_2 + \delta t$.] The ergodic hypothesis requires trajectories to visit “each cell” of phase space of volume h^{3N} , not “each location” in phase space. This avoids the problem of self-intersecting trajectories.

Comparing to $q_{\text{trans,qm}} = \left(\frac{2\pi mkT}{h^2} \right)^{3/2} V$, we see that we need a factor of h^3 in the denominator of $q_{\text{trans,cl}}$. In fact, it turns out that to construct a partition function from a classical Hamiltonian, this h^3 factor is required, so our assumption above must be corrected:

$$\begin{aligned}
 q_{\text{trans,cl}} &= \frac{1}{h^3} \int \dots \int e^{-\epsilon_{\text{classical}}/kT} d\tilde{\mathbf{p}} d\tilde{\mathbf{q}} && \text{(dimensionless)} \\
 Q_{\text{trans,cl}} &= \frac{q_{\text{trans,cl}}^N}{N!} = \frac{1}{N! h^{3N}} \left[\int \int e^{-\epsilon_{\text{classical}}/kT} d\tilde{\mathbf{p}} d\tilde{\mathbf{q}} \right]^N = \frac{V^N}{N!} \left(\frac{2\pi mkT}{h^2} \right)^{3N/2}
 \end{aligned}$$

CONCLUSION: Classical and quantum descriptions of translational degrees of freedom yield consistent results. QM is operating in classical limit because energies of the translational states are so closely spaced that they can be approximated as continuous, as in classical mechanics.



The average molecular translational energy, $\frac{3}{2}kT$, is independent of the kind of molecule, or more precisely, independent of the energy level spacings because these spacings are $\sim 10^{20}$ times smaller than kT . Spacings don't change much from He, to C_6H_6 , to DNA. If T were decreased to 10^{-19} K, then He, C_6H_6 , and DNA would have different \bar{E}_{trans} .

CLASSICAL EQUIPARTITION OF ENERGY PRINCIPLE

Each squared momentum or position term in the energy of a particle contributes $\frac{1}{2}kT$ to the average energy; according to this principle, translation along each coordinate axis contributes $\frac{1}{2}kT$; rotation about each principal axis contributes $\frac{1}{2}kT$; and each vibrational mode contributes kT ($\frac{1}{2}kT$ each for kinetic and potential energy) to the average energy.

$$P(\epsilon) = \frac{g(\epsilon)e^{-\epsilon(p^{3N}, q^{3N})/kT}}{\iint e^{-\epsilon(p^{3N}, q^{3N})/kT} dp^{3N} dq^{3N} / N! h^{3N}}$$

Classical Boltzmann distribution function

$g(\epsilon)$ is the density of states, often denoted as $\rho(\epsilon)$. It has units $(\text{energy})^{-1}$.

$$\bar{\epsilon} = \int_0^{\infty} \epsilon P(\epsilon) d\epsilon = \bar{\epsilon}_x + \bar{\epsilon}_y + \bar{\epsilon}_z = \frac{1}{2}kT + \frac{1}{2}kT + \frac{1}{2}kT = \frac{3}{2}kT$$

INTERNAL DEGREES OF FREEDOM — FACTORIZATION OF Q

ATOMS — have one internal degree of freedom
ELECTRONIC degree of freedom

MOLECULES — have other degrees of freedom

ELECTRONIC, VIBRATION, AND ROTATION, each of which contributes to total energy and to other macroscopic properties.

Nuclear hyperfine? [Nuclear spin degeneracy factors. LATER.]

Internal energy adds to translational energy to get total energy

$$\epsilon = \epsilon_{\text{trans}} + \epsilon_{\text{int}}$$

quantum #'s
internal quantum #'s
N,M,L

where ϵ_{int} = energy from internal degrees of freedom

$$q = \sum_i e^{-\epsilon_i/kT} = \sum e^{-(\epsilon_{\text{trans}} + \epsilon_{\text{int}})/kT}$$

all molecular
states

all molecular
states

We do not have to start over. q_{trans} factors out.

$$q = \left(\sum e^{-\epsilon_{\text{trans}}/kT} \right) \left(\sum e^{-\epsilon_{\text{int}}/kT} \right)$$

translational states

internal states

$$q = q_{\text{trans}} \cdot q_{\text{int}} \quad \leftarrow \quad \text{INTERNAL MOLECULAR PARTITION FUNCTION}$$

$$Q = \frac{(q_{\text{trans}} q_{\text{int}})^N}{N!} = \left(\frac{q_{\text{trans}}}{N!} \right) q_{\text{int}}^N$$

$Q = Q_{\text{trans}} Q_{\text{int}}$	CANONICAL PARTITION FUNCTION
$Q_{\text{trans}} = \frac{Q_{\text{trans}}^N}{N!}$	CANONICAL TRANSLATIONAL PARTITION FUNCTION
$Q_{\text{int}} = Q_{\text{int}}^N$	CANONICAL INTERNAL PARTITION FUNCTION

NOTE: $N!$ was included with Q_{trans} . This is because it's the translational motion that causes the positions of identical particles to be interchanged, requiring the factor of $N!$ The internal motions don't interchange particles.

Classically

$Q_{\text{cl}} = Q_{\text{trans,cl}} Q_{\text{int,cl}}$
$Q_{\text{trans,cl}} = \frac{q_{\text{trans,cl}}^N}{N!} = \frac{[\int e^{-\epsilon_{\text{trans}}/kT} dpdq]^N}{N! h^{3N}}$
$Q_{\text{int,cl}} = q_{\text{int}}^N = \int d\mathbf{p}^{3N} d\mathbf{q}^{3N} e^{-\epsilon_{\text{int}}/kT} / h^{3N}$

CONTRIBUTION OF INTERNAL DEGREES OF FREEDOM TO MACROSCOPIC PROPERTIES

$$\bar{E} = kT^2 \left(\frac{\partial \ln Q}{\partial T} \right)_{N,V} = kT^2 \left(\frac{\partial \ln Q_{\text{trans}} Q_{\text{int}}}{\partial T} \right)_{N,V}$$

$$\bar{E} = kT^2 \left(\frac{\partial \ln Q_{\text{trans}}}{\partial T} \right)_{N,V} + kT^2 \left(\frac{\partial \ln Q_{\text{int}}}{\partial T} \right)_{N,V}$$

$$\bar{E} = \bar{E}_{\text{trans}} + \bar{E}_{\text{int}}$$

(will equipartition be applicable here?)

$$\begin{aligned} A &= -kT \ln Q = -kT \ln Q_{\text{trans}} Q_{\text{int}} \\ &= -kT \ln Q_{\text{trans}} - kT \ln Q_{\text{int}} \\ &= A_{\text{trans}} + A_{\text{int}} \end{aligned}$$

Likewise: $S = S_{\text{trans}} + S_{\text{int}}$

But for pressure: $p = kT \left(\frac{\partial \ln Q}{\partial V} \right)_{N,T} = p_{\text{trans}} + p_{\text{int}} = p_{\text{trans}}$

because no V dependence for internal coordinates

Could use the Classical Mechanical approach to compute any average quantity, e.g.

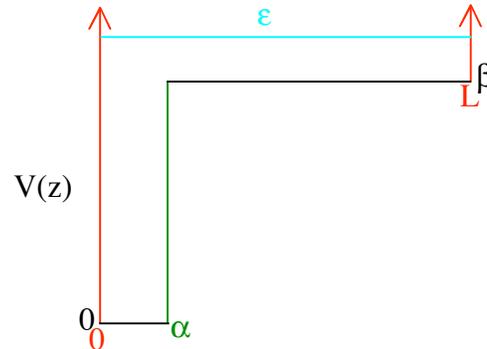
$$\bar{x} = \frac{\int \dots \int d\mathbf{q}^3 d\mathbf{p}^3 x(\mathbf{q}^3, \mathbf{p}^3) e^{-\epsilon(\mathbf{q}^3, \mathbf{p}^3)/kT}}{\int \dots \int d\mathbf{q}^3 d\mathbf{p}^3 e^{-\epsilon(\mathbf{q}^3, \mathbf{p}^3)/kT}}$$

The factors of h^{-3} in numerator and denominator cancel.

The Classical picture will prove extremely useful when there are inter-particle interactions.

Non-Lecture

Example of a classical mechanical calculation: particle bound in a deep well near a solid surface.



$$0 \leq z \leq \alpha$$

$$p_z = [2m\varepsilon]^{1/2}$$

$$\varepsilon_z = p_z^2/2m$$

$$\alpha \leq z \leq L$$

$$p_z = [2m(\varepsilon - \beta)]^{1/2}$$

$$\varepsilon_z = p_z^2/2m + \beta$$

To compute q_{cl} we need

$$\begin{aligned} q_z &= \int_0^L dz \int_{-\infty}^{\infty} dp_z e^{-\varepsilon(z, p_z)/kT} = \int_{-\infty}^{\infty} dp_z \int_0^{\alpha} dz e^{-p_z^2/2mkT} + \int_{-\infty}^{\infty} dp_z \int_{\alpha}^L dz e^{-p_z^2/2mkT} \\ &= [\alpha + (L - \alpha)e^{-\beta/kT}] \int_{-\infty}^{\infty} dp_z e^{-p_z^2/2mkT} \\ &= [\alpha + (L - \alpha)e^{-\beta/kT}] [2\pi mkT]^{1/2} \\ q_z &= [\alpha + (L - \alpha)e^{-\beta/kT}] \left[\frac{2\pi mkT}{h^2} \right]^{1/2} \end{aligned}$$

The multiplicative contributions from the x and y directions do not have the pre-factor

$$q_{cl} = [\alpha + (L - \alpha)e^{-\beta/kT}] \left[\frac{2\pi mkT}{h^2} \right]^{3/2} L^2$$

$$\text{for } kT \gg \beta \quad q_{cl} = \left[\frac{2\pi mkT}{h^2} \right]^{3/2} L^3$$

$$\text{for } kT \ll \beta \quad q_{cl} = \left[\frac{2\pi mkT}{h^2} \right]^{3/2} L^2 \alpha$$

Of course this derivation is not quantitatively correct because it is necessary to assume that $kT \gg \beta$. It is also incorrect because the exact quantum mechanical energy level in the deep, near-surface well is not at the bottom of the well. But this calculation reveals the qualitative change in q_{trans} between the low-T limit (all molecules are adsorbed, thus confined to a volume $L^2\alpha$) and the high-T limit (all molecules are desorbed).