Chapter 7: classical Statistical Mechanics

So far, we have employed QM and considered the high *T* classical limits

Suppose we assume from the beginning that we can describe the system classically?

We conjecture that $q_{cl} \sim \int \cdots \int e^{-\beta H(p,q)} dp dq$

monatomic ideal gas – one atom

$$H = \frac{1}{2m}\left(p_x^2 + p_y^2 + p_z^2\right)$$

$$q_{tr} = \int \cdots \int e^{\frac{-\beta\left(p_x^2 + p_y^2 + p_z^2\right)}{2m}} dp_x dp_y dp_z \underbrace{dx dy dz}_{V}$$

$$q_{tr}^{cl} \sim V\left[\left(\int_{\infty}^{\infty} e^{-\beta p^2/2m} dp\right)\right]^3$$

$$= \left(2\pi mkT\right)^{3/2} V$$

but

$$q_{tr}^{quant} = \left(\frac{2\pi mkT}{h^2}\right)^{3/2} V$$

$$H_{rot} = \frac{1}{2I}\left(p_\theta^2 + \frac{p_\phi^2}{\sin^2\theta}\right)$$

$$q_{rot} \sim \int_{-\infty}^{\infty} dp_\theta dp_\phi \int_0^{2\pi} d\phi \int_0^{\pi} d\theta e^{-\beta H} = 8\pi^2 IkT$$

$$q_{vib} \sim \int_{-\infty}^{\infty} dp \int_{-\infty}^{\infty} dx e^{-\beta H} = \frac{kT}{\upsilon}$$

$$\upsilon = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$$

$$\text{transl. missing } \frac{1}{h^3}; \text{ rot. missing } \frac{1}{h^2}; \text{ vib. missing } \frac{1}{h}$$

Use $$q = \sum_j e^{-\beta\varepsilon_j} \rightarrow \frac{1}{h^s} \int \cdots \int e^{-\beta H} \prod_{j=1}^{s} dp_j dq_j$$

At high enough T $$Q = \frac{q^N}{N!} = \frac{1}{N! h^{sN}} \int \cdots \int e^{-\beta H} \prod_{i=1}^{sN} dp_i dq_i$$

Add appropriate $\frac{1}{h^s}$ correction factor to the classical partition function

We speculate that

$$Q = \frac{1}{N! h^{sN}} \int \cdots \int e^{-\beta H} dpdq$$

H is the classical *n*-body Hamiltonian for a system of Interacting particles

products of all the dp_i, dq_i

Assume that one has a monotonic gas

$$H = \frac{1}{2m} \sum \left({p_{xj}}^2 + {p_{yj}}^2 + {p_{zj}}^2 \right) + U\left(x_1, y_1, z_1, \ldots, x_N, y_N, z_N \right)$$

integrate over momenta

$$Q = \frac{1}{N!}\left(\frac{2\pi mkT}{h^2}\right)^{3N/2} Z_n$$

$$Z_n = \int e^{-U/kT} dx_1 \ldots dz_n =$$ classical configurational $\int$

We already know that it is a poor approximation to treat vibration classically

Divide *H* into classical and quantum parts

$$H = H_{cl} + H_{quant}$$

$$q = q_{cl} q_{quant}$$

$$Q = Q_{cl} Q_{quant}$$

$$= \frac{Q_{quant}}{N!h^{sN}} \int e^{-H_{cl}/kT} dp_{cl} dq_{cl}$$

s now refers to the number of degrees of freedom treated classically

$$\bar{\varepsilon} = \frac{\int\int H e^{-\beta H} dp_1 \ldots dq_s}{\int\int e^{-\beta H} dp_r \ldots dq_s}$$ ← avg. energy for a molecule in a system of independent molecules

In the special case that

$$H = \sum_j^m a_j p_j^2 + \sum_j^n b_j q_j^2 + H\left(p_{m+1}, \ldots p_s, q_{n+1} \ldots q_s\right)$$

$\sum_j^m a_j p_j^2 \rightarrow kT/2$, $\sum_j^n b_j q_j^2 \rightarrow kT/2$ — for each degree of freedom

Equipartition of energy

transl. $= 3/2kT$

rigid rotor $= kT$

harmonic osc. $= kT$ ← valid only at very high T

$$C_\mathrm{v} = \frac{5}{2} Nk + Nk \frac{\frac{\theta_\mathrm{v}^2}{T^2} e^{\theta_\mathrm{v}/\mathrm{T}}}{\left(e^{\theta_\mathrm{v}/T} - 1\right)^2}$$

($\frac{5}{2}Nk$: trans + rot)