

Gibbs quantum statistical mechanics I

Behavior of atoms and molecules is driven by quantum not classical mechanics. Therefore, a system of many atoms or molecules should be described in terms of quantum mechanics.

Introductory remarks

- A classical description of gases breaks down when a typical de Broglie wavelength of gas constituent λ_B is no longer much smaller than a typical inter-constituent distance d . The latter quantity is related to the gas density as $d = \rho^{-1/3}$ and the de Broglie wavelength estimated for an ideal gas is

$$\lambda_B = \frac{h}{p} = \frac{2\pi\hbar}{\sqrt{2mE}} = \frac{2\pi\hbar}{\sqrt{3mk_B T}}. \quad (1)$$

Therefore, the gas can be treated as classical if

$$\rho \left(\frac{4\pi^2\hbar^2}{3mk_B T} \right)^{3/2} \ll 1, \quad (2)$$

otherwise quantum effects are important.

- Measurable quantities – observables – are represented in quantum mechanics by hermitian operators which act in space of states. A goal of quantum statistical mechanics is to compute expectation values of the observables of many-body systems. Having an observable \hat{O} we are interested in

$$\langle \hat{O} \rangle \equiv (\psi, \hat{O}\psi), \quad (3)$$

where ψ is the wave function of N particles and (ψ_1, ψ_2) denotes the scalar product of wave functions ψ_1 and ψ_2 .

- Since the system's hamiltonian \hat{H} is assumed to be time independent the wave function ψ can be written as

$$\psi = \sum_n C_n \varphi_n. \quad (4)$$

where φ_n are the energy eigenfunctions

$$\hat{H}\varphi_n = E_n\varphi_n, \quad (5)$$

and C_n are complex coefficients which depend on time via $e^{i\frac{E_n t}{\hbar}}$. Using the expansion (4), the expectation value (3) equals

$$\langle \hat{O} \rangle = \sum_{n,m} C_n^* C_m (\varphi_n, \hat{O}\varphi_m). \quad (6)$$

- As we already know, statistical mechanics deals with characteristics averaged over microscopically long interval of time τ

$$\overline{\langle \hat{O} \rangle} \equiv \frac{1}{\tau} \int_t^{t+\tau} dt' \langle \hat{O} \rangle = \frac{1}{\tau} \sum_{n,m} (\varphi_n, \hat{O}\varphi_m) \int_t^{t+\tau} dt' C_n^* C_m = \sum_{n,m} (\varphi_n, \hat{O}\varphi_m) \overline{C_n^* C_m}. \quad (7)$$

- There is adopted the postulate of random phases

$$\overline{C_n^* C_m} = 0, \quad \text{if } n \neq m. \quad (8)$$

Thermal environment cancels out an effect of interference of different quantum states.

- Due to the postulate of random phases the expectation value (7) equals

$$\overline{\langle \hat{O} \rangle} = \sum_n \overline{|C_n|^2} (\varphi_n, \hat{O} \varphi_n). \quad (9)$$

- Quantum statistical ensemble is defined via the set of φ_n with the coefficients $\overline{|C_n|^2}$.

Microcanonical ensemble

- Microcanonical ensemble is a set of states of isolated system under consideration and all states with the energy E_n from the interval $[U, U + \delta U]$ are equally probable ($|C_n|^2 = 1$).
- $\Gamma_N(U, V)$ is the number of states φ_n which obey $U \leq E_n \leq U + \delta U$.
- The entropy is defined as in the classical case that is

$$S(U, V) \equiv k_B \ln \Gamma_N(U, V). \quad (10)$$

- At $T = 0$ the system is in its ground state and $\Gamma_N(U, V)$ equals the ground-state degeneracy \mathcal{N} . Therefore,

$$S(T = 0, V) \equiv k_B \ln \mathcal{N}. \quad (11)$$

- According to the third principle of thermodynamics, the entropy vanishes at $T = 0$ which means $S(T = 0, V) \ll k_B N$. To fulfill the principle \mathcal{N} cannot be bigger than N^k with $k \ll N$.

Canonical ensemble

- Canonical ensemble is a set of states of a system which is in thermal contact with a heat bath and

$$\overline{|C_n|^2} \sim e^{-\beta E_n}, \quad (12)$$

where $\beta \equiv \frac{1}{k_B T}$.

- Partition functions is defined as

$$Q_N(T, V) \equiv \sum_n e^{-\beta E_n}. \quad (13)$$

- The relation with thermodynamics is established by means of the relations

$$U(T, V) \equiv \frac{1}{Q_N(T, V)} \sum_n E_n e^{-\beta E_n}, \quad (14)$$

$$F(T, V) \equiv -k_B T \ln Q_N(T, V). \quad (15)$$

where F is the free energy, $F = U - TS$.

Grand canonical ensemble

- Grand canonical ensemble is a set of states of a system which exchanges heat and particles with its environment and

$$\overline{|C_n|^2} \sim e^{-\beta(E_n - \mu N)}, \quad (16)$$

where μ is the chemical potential.

- The grand partition function is

$$\Xi(T, V, \mu) = \sum_{N=0}^{\infty} z^N Q_N(T, V), \quad (17)$$

where $z \equiv e^{\beta\mu}$.

- The relation with thermodynamics is established by means of the relations

$$U = -\frac{\partial}{\partial\beta} \ln \Xi(T, V, z), \quad (18)$$

$$\langle N \rangle = z \frac{\partial}{\partial z} \ln \Xi(T, V, z), \quad (19)$$

$$pV = k_B T \ln \Xi(T, V, z). \quad (20)$$

Einstein's model of crystal

The crystal is treated as a system N independent quantum harmonic oscillators.

- The energy of a single oscillator is $E_n = \hbar\omega(n + \frac{1}{2})$, where $n = 0, 1, 2, \dots$
- The energy of N oscillators is $E_{n_1} + E_{n_2} + \dots + E_{n_N}$ and

$$\begin{aligned} Q_N(T, V) &= \sum_{n_1=0}^{\infty} \sum_{n_2=0}^{\infty} \dots \sum_{n_N=0}^{\infty} e^{-\beta(E_{n_1} + E_{n_2} + \dots + E_{n_N})} = \sum_{n_1=0}^{\infty} e^{-\beta E_{n_1}} \sum_{n_2=0}^{\infty} e^{-\beta E_{n_2}} \dots \sum_{n_N=0}^{\infty} e^{-\beta E_{n_N}} \\ &= \left(\sum_{n=0}^{\infty} e^{-\beta\hbar\omega(n + \frac{1}{2})} \right)^N = \left(e^{-\frac{\beta\hbar\omega}{2}} \sum_{n=0}^{\infty} e^{-\beta\hbar\omega n} \right)^N = \left(\frac{e^{-\frac{\beta\hbar\omega}{2}}}{e^{\beta\hbar\omega} - 1} \right)^N, \end{aligned} \quad (21)$$

where the formula

$$\sum_{n=0}^{\infty} q^n = \frac{1}{1 - q} \quad (22)$$

is used.

- The crystal's energy is

$$U = -\frac{\partial}{\partial\beta} \ln Q_N(T, V) = N \left(\frac{\hbar\omega}{e^{\beta\hbar\omega} - 1} + \frac{\hbar\omega}{2} \right), \quad (23)$$

where the second term corresponds to the so-called *zero-point fluctuations*.

- The heat capacity equals

$$C_V = \left(\frac{\partial U}{\partial T} \right)_V = \frac{N}{k_B T^2} \frac{(\hbar\omega)^2 e^{\beta\hbar\omega}}{(e^{\beta\hbar\omega} - 1)^2}, \quad (24)$$

which can be approximated as

$$C_V \approx \begin{cases} Nk_B & \text{for } k_B T \gg \hbar\omega, \\ \frac{N(\hbar\omega)^2}{k_B T^2} e^{-\beta\hbar\omega} & \text{for } k_B T \ll \hbar\omega. \end{cases} \quad (25)$$

The heat capacity as a function of temperature is shown in Fig. 1.

- When $T \rightarrow 0$ the heat capacity vanishes in agreement with the third principle of thermodynamics.
- If the oscillations occur in three dimensions, N should be replaced by $3N$.

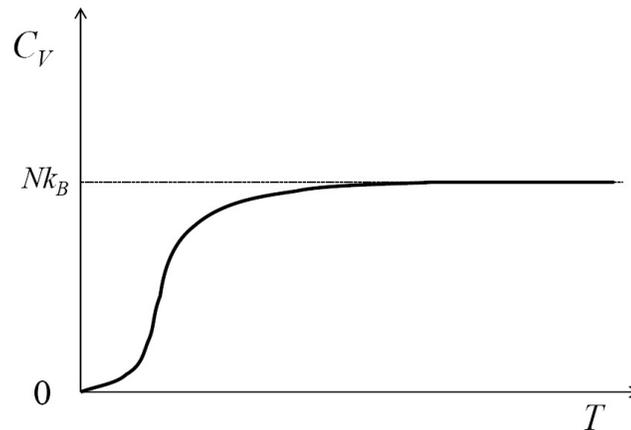


Figure 1: Heat capacity as a function of temperature