Quantum Statistical Mechanics

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November 13, 2018

Bose-Einstein Distribution and Density of States

Now, we have all ingredients to analyze photon statistics,

$$\langle n \rangle = \frac{1}{e^{\beta(\epsilon-\mu)} - 1},$$

$$\epsilon = \int_0^\infty \frac{\epsilon g(\epsilon) d\epsilon}{e^{\beta(\epsilon-\mu)} \pm 1},$$

$$g(\omega) d\omega = 2 \times \frac{V\omega^2}{2\pi^2 c^3} d\omega.$$

Photon Gases

Photons can be created or destroyed freely, meaning that the chemical potential μ of photons is zero. Thus, the number of photons per eigenstate with frequency ω is

$$\begin{aligned}\langle n_\omega \rangle &= \frac{1}{e^{\beta(\epsilon_w - \mu)} - 1} \\ &= \frac{1}{e^{\beta\hbar\omega} - 1}.\end{aligned}$$

Note that the same form is derived from the statistics of quantum harmonic oscillators. The number of photons in a given frequency interval is given by

$$\begin{aligned}n_\omega d\omega &= g(\omega) n(\omega) d\omega \\ &= 2 \times \frac{V\omega^2}{2\pi^2 c^3} \times \frac{1}{e^{\beta\hbar\omega} - 1} d\omega.\end{aligned}$$

Black-Body Radiation

The energy per unit frequency interval is

$$U(\omega)d\omega = \hbar\omega \times 2 \times \frac{V\omega^2}{2\pi^2 c^3} \times \frac{1}{e^{\beta\hbar\omega} - 1} d\omega.$$

The total energy of the radiation in a box is then

$$U = \frac{V\hbar}{\pi^2 c^3} \int_0^\infty \frac{\omega^3}{e^{\beta\hbar\omega} - 1} d\omega.$$

This is Planck's formula for black-body radiation.

Black-Body Radiation

Let $x = \beta\hbar\omega$, we obtain

$$U = \frac{V\hbar}{\pi^2 c^3}\left(\frac{1}{\beta\hbar}\right)^4 \int_0^\infty \frac{x^3}{e^x - 1} dx.$$

This integral is not simple, but fortunately we can obtain the exact value as $\int_0^\infty \frac{x^3}{e^x-1} dx = \frac{\pi^4}{15}$. Therefore, the energy is

$$U = \frac{\pi^2 V k_B^4}{15\hbar^3 c^3} T^4.$$

Thus, the energy flux follows Stefan-Boltzmann's Law:

$$\eta = \sigma T^4. \tag{1}$$

Black-Body Radiation

Planck's formula for black-body radiation is

$$\frac{U}{V} = \frac{\hbar}{\pi^2 c^3} \int_0^\infty \frac{\omega^3}{e^{\beta\hbar\omega} - 1} d\omega = \int_0^\infty u_\omega d\omega.$$

We define u_ω as the spectral energy density,

$$u_\omega = \frac{\hbar}{\pi^2 c^3} \frac{\omega^3}{e^{\beta\hbar\omega} - 1}.$$

- At low frequency: $e^{\beta\hbar\omega} \approx 1 + \beta\hbar\omega$, we recover the Rayleigh-Jeans formula (and also equipartition theorem)

$$u_\omega \approx \frac{1}{\pi^2 c^3} \frac{\omega^2}{\beta} \sim k_B T.$$

- At high frequency: $1/(e^{\beta\hbar\omega} - 1) \approx e^{-\beta\hbar\omega}$, we can remedy the ultraviolet catastrophe

$$u_\omega \approx \frac{\hbar}{\pi^2 c^3} \omega^3 e^{-\beta\hbar\omega}.$$

Phonons are quantized thermal waves in a solid. Like photon (quantized electromagnetic waves), they obey a wave equation:

$$\nabla^2 \psi = \frac{1}{v^2} \frac{\partial^2 \psi}{\partial t^2}.$$

We already have all ingredients to analyze phonon statistics,

$$\langle n \rangle = \frac{1}{e^{\beta(\epsilon - \mu)} - 1},$$

$$g(\omega) d\omega = 3 \times \frac{V\omega^2}{2\pi^2 v^3} d\omega.$$

Harmonic Solid

At equilibrium, N atoms in a solid can be described by atoms in a harmonic potential (for more details, take solid-state physics course). Therefore, the energy is

$$E = \sum_{i}^{3N} \hbar\omega_i \left(n_i + \frac{1}{2} \right)$$

Since phonons are bosons, we can apply Bose-Einstein statistics with $\mu = 0$ (thermal phonons can be created or destroyed by random energy fluctuations),

$$E = \sum_{i}^{3N} \hbar\omega_i \left(\frac{1}{e^{\beta\hbar\omega_i} - 1} + \frac{1}{2} \right).$$

Einstein Model ($\omega_i = \omega$)

When all modes have the same frequency, we can simply calculate the energy

$$
\begin{aligned}
E &= \sum_i^{3N} \hbar\omega \left(\frac{1}{e^{\beta\hbar\omega} - 1} + \frac{1}{2} \right) \\
&= \frac{3N}{2}\hbar\omega + 3N \frac{\hbar\omega}{e^{\beta\hbar\omega} - 1}.
\end{aligned}
$$

When $T \approx 0$ (low temperature),

$$C_v \sim T^{-2} e^{-1/T}.$$

When $T \to \infty$ (high temperature),

$$C_v \sim 3Nk_B.$$

There should be the maximum frequency ω_D due to the smallest wave length as the spacing between atoms. It is impossible for sound waves to propagate through a solid with wavelength smaller than the atomic spacing (frequency larger than $\sim 1/\lambda$. Then,

$$\int_0^{\omega_D} d\omega g(\omega) = \int_0^{\omega_D} d\omega \left(3 \times \frac{V\omega^2}{2\pi^2 v^3}\right) = 3N,$$

and it gives

$$\omega_D = \left(\frac{6N\pi^2 v^3}{V}\right)^{1/3}.$$

Debye Model

The energy is then

$$
\begin{aligned}
E &= \int_0^{\omega_D} d\omega g(\omega)\hbar\omega \left(\frac{1}{e^{\beta\hbar\omega_i} - 1} + \frac{1}{2} \right) \\
&= \frac{3V\hbar}{2\pi^2 v^3} \int_0^{\omega_D} d\omega\omega^3 \left(\frac{1}{e^{\beta\hbar\omega_i} - 1} + \frac{1}{2} \right) \\
&\approx \frac{3V\hbar}{2\pi^2 v^3} \int_0^{\omega_D} d\omega \frac{\omega^3}{e^{\beta\hbar\omega_i} - 1}
\end{aligned}
$$

Letting $x = \beta\hbar\omega$ and $x_D = T_D/T$, we have

$$
E = \frac{3V\hbar}{2\pi^2(\hbar v)^3} (k_B T)^4 \int_0^{T_D/T} d\omega \frac{x^3}{x - 1}.
$$

Debye Model

$$E = \frac{3V\hbar}{2\pi^2(\hbar v)^3}(k_B T)^4 \int_0^{T_D/T} d\omega \frac{x^3}{x-1}.$$

When $T \ll T_D$ (low temperature),

$$\int_0^{T_D/T} d\omega \frac{x^3}{x-1} \approx \int_0^{\infty} d\omega \frac{x^3}{x-1} = \frac{\pi^4}{15},$$

$$C_v = \frac{\partial E}{\partial T} \sim T^3.$$

When $T \gg T_D$ (high temperature),

$$\int_0^{T_D/T} d\omega \frac{x^3}{x-1} \approx \int_0^{T_D/T} d\omega (x^2 + \cdots) = \frac{1}{3}\left(\frac{T_D}{T}\right)^3 + \cdots$$

$$C_v = \frac{\partial E}{\partial T} \sim 3Nk_B.$$

Bose-Einstein Condensation

Check the total number of bosons with $\mu = 0$,

$$N = \int_0^\infty g(\epsilon) \frac{1}{e^{\beta\epsilon} - 1} d\epsilon$$
$$= \frac{V m^{3/2}}{\sqrt{2}\pi^2 \hbar^3} \int_0^\infty \frac{\sqrt{\epsilon}}{e^{\beta\epsilon} - 1} d\epsilon$$
$$= V \left(\frac{\sqrt{2\pi m k_B T}}{h} \right)^3 \frac{2}{\sqrt{\pi}} \int_0^\infty \frac{\sqrt{z}}{e^z - 1} dz.$$

where $z = \beta\epsilon$ and $\lambda = \frac{h}{\sqrt{2\pi m k_B T}}$ is the thermal de Broglie wavelength. By using the Riemann zeta function as

$$\zeta(s) = \frac{1}{\Gamma(s)} \int_0^\infty \frac{z^{s-1}}{e^z - 1} dz,$$

we obtain

$$N = \left(\frac{V}{\lambda^3} \right) \zeta(3/2).$$

What does it mean?

$$\frac{N_{max}}{V} = \frac{\zeta(3/2)}{\lambda^3} \approx \frac{2.612}{\lambda^3}$$

- Should there be the maximum number of bosons? No.
- Our approximation of the distribution of eigenstates as a continuum breaks down if we try to put more particles in. In other words, all the particles more than N_{max} will be in the ground state.
- This phenomenon is called Bose-Einstein Condensation, first predicted in 1924 and experimentally confirmed in 1995.

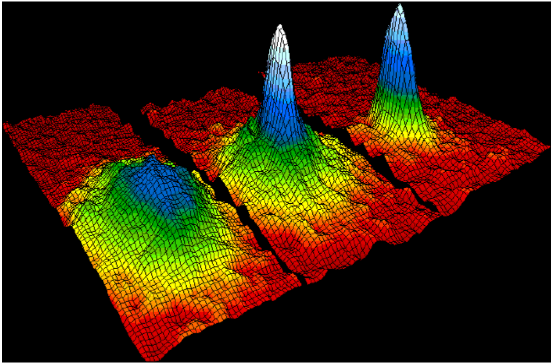
Bose-Einstein Condensation

When and why does it happen?

$$k_B T_c^{(BEC)} = \frac{h^2}{2\pi m} \left(\frac{N}{V\zeta(3/2)} \right)^{3/2} .$$

When the distance between μ and the lowest energy level ϵ_0 is significantly smaller than the distance between the lowest and the second lowest energy level ϵ_1, the continuum approximation becomes qualitatively wrong. Then, the lowest state (ground state) absorbs all the extra particles beyond N_{max}.

Bose-Einstein Condensation



Velocity-distribution for a gas of rubidium atoms, confirming the Bose-Einstein Condensation [from Wikipedia].

Electrons in a Metal

Consider electrons in a metal as free non-interacting electrons.

$$\langle n \rangle = \frac{1}{e^{\beta(\epsilon-\mu)}+1},$$
$$\epsilon = \frac{\hbar^2 k^2}{2m},$$
$$g(\epsilon)d\epsilon = \frac{mV}{\pi^2\hbar^3}\sqrt{2m\epsilon}d\epsilon.$$

Electrons in a Metal

Then, the total number of electrons is

$$N = \int_0^\infty g(\epsilon)\langle n\rangle d\epsilon,$$
$$\langle n\rangle = \frac{1}{e^{\beta(\epsilon-\mu)}+1}.$$

At $T = 0$ (equivalently $\beta \to \infty$),

- When $\epsilon \leq \mu$, $\langle n\rangle = 1$.
- When $\epsilon > \mu$, $\langle n\rangle = 0$.

Fermi Energy

We define the zero temperature value of chemical potential as Fermi energy ϵ_F. It plays an important role to analyze the (electrical) property of solids. And, we can obtain the total number of particles by using ϵ_F as

$$
\begin{aligned}
N &= \int_0^\infty g(\epsilon)\langle n\rangle d\epsilon \\
&= \int_0^{\epsilon_F} g(\epsilon) d\epsilon \\
&= \int_0^{\epsilon_F} \frac{mV}{\pi^2\hbar^3}\sqrt{2m\epsilon}\,d\epsilon \\
&= \frac{(2\epsilon_F m)^{3/2}}{3\pi^2\hbar^3}V.
\end{aligned}
$$

This approximation is not accurate in general because we assume independent free particles, but it is surprisingly useful as the simplest example.

Degeneracy Pressure

The Fermi energy is then

$$\epsilon_F = \frac{\hbar^2}{2m}(3\pi^2 N/V)^{2/3} \sim \left(\frac{N}{V}\right)^{2/3}.$$

The energy is

$$E = \int_0^{\epsilon_F} \epsilon g(\epsilon) d\epsilon = \int_0^{\epsilon_F} \epsilon \frac{mV}{\pi^2\hbar^3}\sqrt{2m\epsilon}d\epsilon$$
$$\sim V\epsilon_F^{5/2} = V\left(\frac{N}{V}\right)^{5/3}.$$

The degeneracy pressure is

$$P \sim \frac{E}{V} = \left(\frac{N}{V}\right)^{5/3} = \rho^{5/3}.$$