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Theory 4. Statistical Physics.
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January 28, 2024.
Lecture 23.

Last time: Legendre transforms briefly
Cumulant expansion + first introduction to interacting models.

Today:
Photon gas, blackbody radiation
Ultraviolet catastrophe
Virial expansion, start real gases + van der Waals eqn.

Before we analyze interacting models, it is worthwhile to discuss the remaining non-interacting systems of photons (massless gas of particles) and phonons (collective modes/vibrational modes of crystal lattices/solids).

Recap: photons are particles that ~~obey~~ have wave-like properties according to their wave number k.

$$E = \hbar\omega = h\nu, \quad k = \frac{\omega}{c}, \quad k = \frac{2\pi}{\lambda}, \text{ momentum } p = \hbar k.$$

If we have a cubic box of $V = L^3$, then the density of states (in momentum space) is

$$g(k)\,dk = \frac{4\pi k^2 dk}{(2\pi/L)^3} \cdot 2,$$

where the factor of 2 corresponds to two transverse polarizations of each photon.

$$\Rightarrow g(k) = \frac{V k^2 dk}{\pi^2}, \quad g(\omega) = g(k)\frac{dk}{d\omega} = \frac{g(k)}{c}$$

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

Recall that simple harmonic oscillator gives

$$E_{sys} = \int_0^\infty g(\omega)\, d\omega \cdot \hbar\omega\left(\frac{1}{2} + \frac{1}{e^{\beta\hbar\omega}-1}\right)$$

We must discard the zero pt. energy as an infinite constant.

$$E_{sys} = \int_0^\infty g(\omega)\, d\omega \frac{\hbar\omega}{e^{\beta\hbar\omega}-1} = \frac{V\hbar}{\pi^2 c^3}\int_0^\infty \frac{\omega^3\, d\omega}{e^{\beta\hbar\omega}-1}$$

Use $x = \hbar\beta\omega$, so

$$E_{sys} = \frac{V\hbar}{\pi^2 c^3}\left(\frac{1}{\hbar\beta}\right)^4 \int_0^\infty \frac{x^3\, dx}{e^x-1} = \left(\frac{V\pi^2 k_B^4}{15 c^3\hbar^3}\right) T^4$$

$$\int_0^\infty \frac{x^3\, dx}{e^x-1} = \zeta(4)\Gamma(4) = \frac{\pi^4}{15}.$$

The energy density $u = \frac{E_{sys}}{V} = A T^4$,

$$A = \frac{\pi^2 k_B^4}{15 c^3 \hbar^3}, \quad \text{and} \quad A = \frac{4\sigma}{c}, \text{ with}$$

Stefan-Boltzmann const. $\sigma = \frac{\pi^2 k_B^4}{60 c^2 \hbar^3} \simeq 5.67 \cdot 10^{-8} \frac{W}{m^2 K^4}$.

The Stefan-Boltzmann law is that the power per unit area for photons at an equilibrium temperature T is σT^4, i.e. proportional to T^4.

(Note, this essentially stems from the fact that the pressure of the photon gas is $\frac{u}{3}$ instead of $p = \frac{2u}{3}$ as for a massive gas)

We can further write

$$u = \frac{E_{sys}}{V} = \int u_\omega \, d\omega \text{, with}$$

u_ω = spectral energy density function

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

is the black-body distribution.

Intuitively, spectral energy density tells you how the energy density is distributed in spectra, i.e. across angular frequencies.

Can also write $\omega = 2\pi\nu$, $u_\omega d\omega = u_\nu d\nu$,

$$\Rightarrow u_\nu = \frac{8\pi h}{c^3} \frac{\nu^3}{e^{\beta h\nu} - 1}$$

and $u_\nu |d\nu| = u_\lambda |d\lambda|$, $\nu = \frac{c}{\lambda}$, $\frac{d\nu}{d\lambda} = \frac{-c}{\lambda^2}$

$$\Rightarrow u_\lambda = \frac{8\pi hc}{\lambda^5} \frac{1}{e^{\beta hc/\lambda} - 1}$$

Remarks:

At low frequency $\simeq$ long wavelength, $\frac{h\nu}{k_B T} \ll 1$,

then $e^{\beta h\nu} \simeq 1 + \frac{h\nu}{k_B T}$, $u_\nu \simeq \frac{8\pi h}{c^3} \frac{\nu^3 k_B T}{h\nu}$

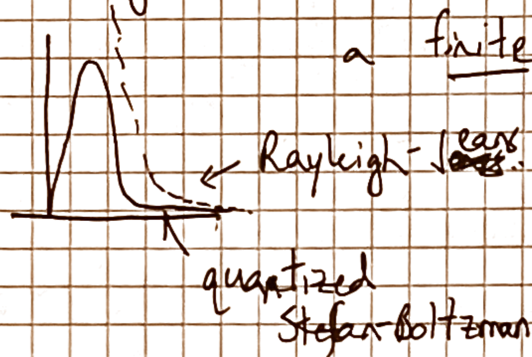
$$= 8\pi \frac{\nu^2}{c^3} k_B T$$

and $u_\lambda = \frac{8\pi k_B T}{\lambda^4}$.

These are Rayleigh-Jeans laws for radiation spectral energy densities, which do not account for quantization of photon energies. (No Planck's const.)

Using these expressions leads to an ultraviolet catastrophe, since $u = \int_0^\infty \frac{8\pi k_B T \, d\lambda}{\lambda^4} \to \infty$.

In other words, the quantization of energy modes prevents the divergence for high energy / small wavelength modes. Thus the correct expression gives a finite energy density, $u = \frac{4\sigma}{c} T^4$.



Practical aspects:

Cosmic microwave background:

T of universe is not zero. Instead, we are enveloped in a thermal bath of photons with $T \sim 2.7K$.

Another practical aspect:

Einstein A + B coefficients for photons to transition thermally between two levels: Given an additional radiation field that provides a spectral flux of photons, the populations of the two levels can become inverted, leading to a laser.

Phonons.

Another canonical example of non-interacting systems are vibrational modes of a lattice. In the Einstein model, all vibrational modes have same frequency ω_E, and we have $3N$ modes: if independent & non-interacting we treat as harmonic oscillators,

$$Z = \prod_{k=1}^{3N} Z_k \,, \qquad \ln Z = \sum_{k=1}^{3N} \ln Z_k$$

$$Z_k = \sum_{n=0}^{\infty} e^{-(n+\frac{1}{2})\hbar\omega_E\beta} = \frac{e^{-\frac{1}{2}\hbar\omega_E\beta}}{1-e^{-\hbar\omega_E\beta}} .$$

Can see $\ln Z = 3N\left[-\frac{1}{2}\hbar\omega_E\beta - \ln\left(1-e^{-\hbar\omega_E\beta}\right)\right]$

and $E_{sys} = -\left(\frac{\partial \ln Z}{\partial \beta}\right) = \frac{3N}{2}\hbar\omega_E + \frac{3N\hbar\omega_E}{e^{\hbar\omega_E\beta}-1} .$

We can define an empirical temperature Θ_E,

$$\hbar\omega_E = k_B\Theta_E ,$$

$$E_{sys} = 3R\,\Theta_E\left[\frac{1}{2} + \frac{1}{e^{\Theta_E/T}-1}\right] .$$

per mole of solid

A more complicated model is Debye model, which allows vibrational modes to follow lattice vibrations indexed by wave number but all sharing the same sound speed.

[Get $g(\omega)\,d\omega = \frac{9N\omega^2 d\omega}{\omega_D^3}$,

$$\omega_D \equiv \left(\frac{6N\pi^2 v_s^3}{V}\right)^{1/3} \Big]$$

Finally, can lift the assumption of fixed speed of sound and allow a nontrivial dispersion relation for $\frac{d\omega}{dk}$ of the vibrational modes.

[$\omega = \left(\frac{4K}{m}\right)^{1/2}\left|\sin\left(\frac{qa}{2}\right)\right|$, K is force constant for string of atoms, a is atomic spacing.

Real gases, virial coefficients, van der Waals equation of state.

We have now seen the impact and limitations of quantization on systems ignoring interactions.

Unfortunately, the set of systems with interactions that admit an exact treatment from stat. physics techniques is essentially non-existent, since (i.e.) in the canonical ensemble, we would need to solve the (quantum) Hamiltonian for the exact energy eigenvalues. As experience tells us, exactly solvable Hamiltonians are essentially non-existent, so we usually have to deal with harmonic oscillators + perturbation theory or artificial/idealized potentials and add deformations.

The formal methodology to handle perturbation theory in stat. physics is the cumulant expansion, where moments are associated with a series expansion around well-defined (and idealized/exact) equilibrium expectation values.

We can build intuition for the cumulant expansion by studying corrections to the ideal gas law as a series expansion: the virial expansion:

$$\frac{pV_m}{RT} = 1 + \frac{B}{V_m} + \frac{C}{V_m^2} + \dots$$

Will discuss more & van der Waals gas next time.