Quantum statistics

- **Black-body radiation.** Phonons correspond to vibrations of a solid medium. The vibrations of electromagnetic (EM) field are called *photons*. The Hamiltonian for the EM field can also be written as a sum of harmonic oscillators

$$\mathcal{H}=\frac{1}{2}\sum_{\vec{k},\alpha}\left[\left|\tilde{p}_{\vec{k},\alpha}\right|^2+\omega_\alpha(\vec{k})^2\left|\tilde{u}_\alpha(\vec{k})\right|^2\right]$$

$$\mathcal{H}_{solid}=\mathcal{V}^*+\sum_{\vec{k},\alpha}\left[\frac{1}{2m}\left|\tilde{p}_\alpha(\vec{k})\right|^2+\frac{\tilde{K}(\vec{k})}{2}\left|\tilde{u}_\alpha(\vec{k})\right|^2\right]$$

Photons, $\omega_\alpha(\vec{k})=ck$, where c is the light speed.

Debye model $\omega(\vec{k})=vk$, where v is the speed of sound in the crystal.

- **Periodic boundary conditions.** The allowed wavevectors in a box of size L are where n_x, n_y, and n_z are integers.

$$\vec{k}=\left(\frac{2\pi n_x}{L_x},\frac{2\pi n_y}{L_y},\frac{2\pi n_z}{L_z}\right),$$

Solid: $T_D=\frac{\hbar v k_{\max}}{k_B}\approx\frac{\hbar v}{k_B}\cdot\frac{\pi}{a}$

For $T\gg T_D$, $3N$ modes of k_BT.

Photon: $k_{\max}=?$ Mode number of k_BT?

- **Ultraviolet catastrophe.** However, in classical treatments, there is no limit to the wavevector, assigning k_BT per mode leads to an infinite energy. This is called ultraviolet catastrophe.

Quantum statistics

- **Quantized energy levels.** Ultraviolet catastrophe was solved when Planck suggested the allowed values of EM energy must be quantized

$$\mathcal{H}^q = \sum_{\vec{k},\alpha} \hbar c k \left(n_\alpha(\vec{k}) + \frac{1}{2} \right), \quad \text{with} \quad n_\alpha(\vec{k}) = 0, 1, 2, \cdots$$

- **Energy.** Since the dispersion of photons is linear, the energy of photons is very similar to the results of low-temperature limit of Debye model.

$$E_{photon} = \left\langle \mathcal{H}^q \right\rangle = V E_0 + \frac{2V}{(2\pi)^3} \int_0^\infty \mathrm{d}^3\vec{k} \, \frac{\hbar c k}{\mathrm{e}^{\beta \hbar c k} - 1}, \qquad E_{solid} \underset{T \ll T_D}{\approx} E_0 + \int_0^\infty \frac{3V}{(2\pi)^3} \mathrm{d}^3\vec{k} \, \frac{\hbar v k}{\mathrm{e}^{\beta \hbar v k} - 1}$$

Factor “2” of *V* is due to the 2 degree of freedom of polarizations. Define energy density

$$E^* = E - V E_0$$

$$\frac{E^*}{V} = \frac{\hbar c}{\pi^2} \left(\frac{k_B T}{\hbar c} \right)^4 \int_0^\infty \frac{\mathrm{d}x x^3}{\mathrm{e}^x - 1} = \frac{\pi^2}{15} \frac{(k_B T)^4}{(\hbar c)^3}$$

Similar to the low-*T* limit of Debye model.

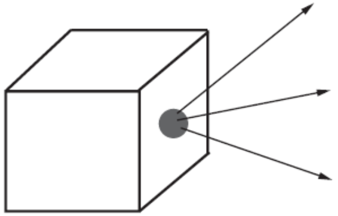
$$x = \beta \hbar c |\vec{k}|,$$

$$\mathrm{d}^3\vec{k} = 4\pi x^2 \, \mathrm{d}x / (\beta \hbar c)^3$$

$$\int_0^\infty \frac{x^3}{e^x - 1} \mathrm{d}x = \frac{\pi^4}{15}$$

Quantum statistics

- ❑ **Stefan–Boltzmann law.** If a hole is opened in the container wall, the escaping energy flux per unit area and per unit time is



the average of the component of the velocity perpendicular to the hole (your homework)

$$\phi = \langle c_\perp \rangle \frac{E}{V}. \quad \langle c_\perp \rangle = \frac{c}{4},$$

$$\frac{E^*}{V} = \frac{\pi^2}{15}\frac{(k_B T)^4}{(\hbar c)^3} \qquad \phi = \frac{1}{4}c\frac{E}{V} = \frac{\pi^2}{60}\frac{k_B^4 T^4}{\hbar^3 c^2}$$

- ❑ **Radiation Pressure.** Photons have kinetic momentum; they can exert pressure on an object. In order to calculate the pressure, let’s look at the partition function

$$P = -\left.\frac{\partial F}{\partial V}\right|_T \qquad F = -k_B T \ln Z \qquad Z = \sum_{\{n_\alpha(\vec{k})\}} \prod_{\vec{k},\alpha} \exp\left[-\beta\hbar\omega(\vec{k})\left(n_\alpha(\vec{k}) + \frac{1}{2}\right)\right] = \prod_{\vec{k},\alpha} \frac{\mathrm{e}^{-\beta\hbar ck/2}}{1-\mathrm{e}^{-\beta\hbar ck}}$$

Free energy is

$$F = -k_B T \ln Z \; = k_B T \sum_{\vec{k},\alpha}\left[\frac{\beta\hbar ck}{2} + \ln\left(1-\mathrm{e}^{-\beta\hbar ck}\right)\right] = 2V\int \frac{\mathrm{d}^3\vec{k}}{(2\pi)^3}\left[\frac{\hbar ck}{2} + k_B T \ln\left(1-\mathrm{e}^{-\beta\hbar ck}\right)\right]$$

Quantum statistics

- **Radiation Pressure.**

$$F = 2V\int\frac{\mathrm{d}^3\vec{k}}{(2\pi)^3}\left[\frac{\hbar ck}{2} + k_B T\ln\left(1-\mathrm{e}^{-\beta\hbar ck}\right)\right]$$

$$P = -\left.\frac{\partial F}{\partial V}\right|_T = -\int\frac{\mathrm{d}^3\vec{k}}{(2\pi)^3}\left[\hbar ck + 2k_B T\ln\left(1-\mathrm{e}^{-\beta\hbar ck}\right)\right]$$

$$\mathrm{d}^3\vec{k} = 4\pi k^2\,\mathrm{dk}$$

$$= P_0 - \frac{k_B T}{\pi^2}\int_0^\infty \mathrm{d}k k^2 \ln\left(1-\mathrm{e}^{-\beta\hbar ck}\right)$$

Integrate by parts: $\int v du = uv - \int u dv$

$$= P_0 - \frac{k_B T}{\pi^2}\int_0^\infty \ln\left(1-\mathrm{e}^{-\beta\hbar ck}\right)\mathrm{d}\left(\frac{k^3}{3}\right)$$

$$u = \frac{k^3}{3}, \qquad v = \ln\left[1-\exp(-\beta\hbar ck)\right]$$

$$= P_0 + \frac{k_B T}{\pi^2}\int_0^\infty \frac{k^3}{3}\left(\frac{\beta\hbar c\mathrm{e}^{-\beta\hbar ck}}{1-\mathrm{e}^{-\beta\hbar ck}}\right)\mathrm{d}k$$

$$x = \beta\hbar c\,|\vec{k}\,|,$$

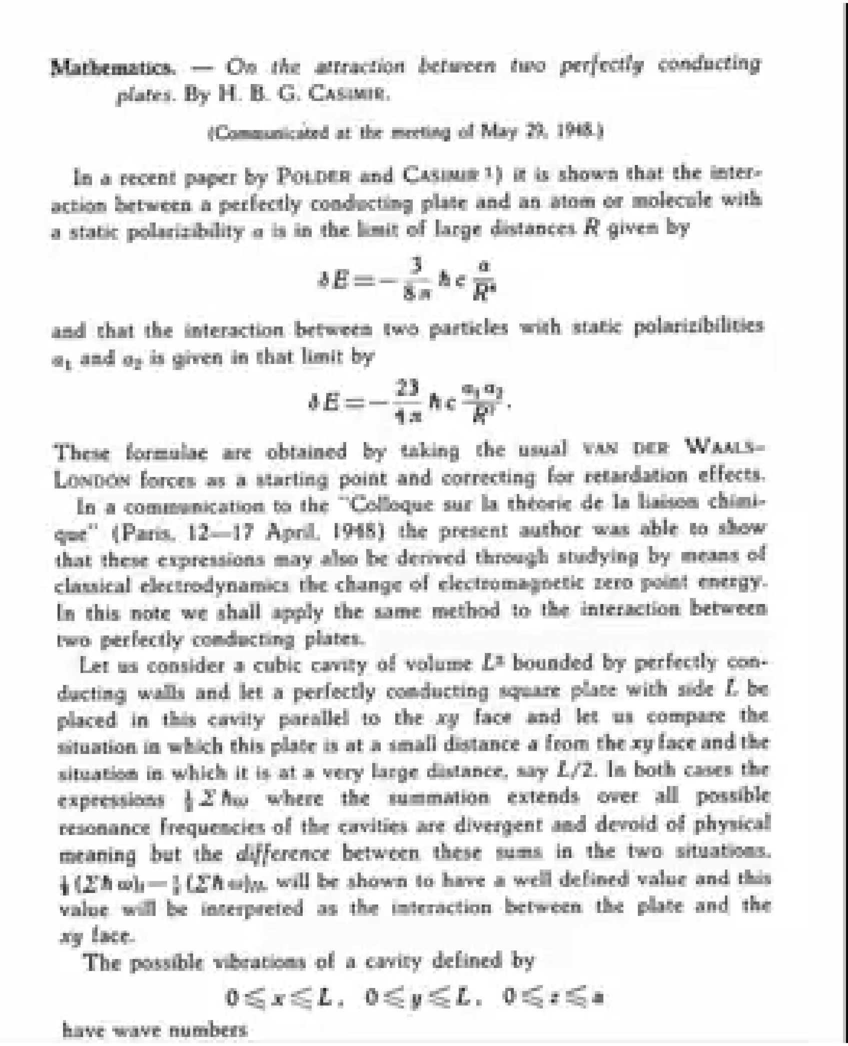
$$\frac{E^*}{V} = \frac{\hbar c}{\pi^2}\left(\frac{k_B T}{\hbar c}\right)^4\int_0^\infty\frac{\mathrm{d}x x^3}{\mathrm{e}^x - 1}$$

$$= P_0 + \frac{k_B T}{3\pi^2(\beta\hbar c)^3}\int_0^\infty \mathrm{d}x x^3\,\frac{\mathrm{e}^{-x}}{1-\mathrm{e}^{-x}} = P_0 + \frac{1}{3}\frac{E}{V}.$$

1/3 is due to relativistic

Note that there is also a zero-point pressure P_0. Differences in this pressure lead to the *Casimir force* between conducting plates, which is measurable.

Casimir force



Mathematics. — *On the attraction between two perfectly conducting plates.* By H. B. G. CASIMIR.

(Communicated at the meeting of May 29, 1948.)

In a recent paper by POLDER and CASIMIR 1) it is shown that the interaction between a perfectly conducting plate and an atom or molecule with a static polarizibility α is in the limit of large distances R given by

$$\delta E = -\frac{3}{8\pi} \hbar c \frac{\alpha}{R^4}$$

and that the interaction between two particles with static polarizibilities α_1 and α_2 is given in that limit by

$$\delta E = -\frac{23}{4\pi} \hbar c \frac{\alpha_1 \alpha_2}{R^7}.$$

These formulae are obtained by taking the usual VAN DER WAALS-LONDON forces as a starting point and correcting for retardation effects.

In a communication to the "Colloque sur la théorie de la liaison chimique" (Paris, 12—17 April, 1948) the present author was able to show that these expressions may also be derived through studying by means of classical electrodynamics the change of electromagnetic zero point energy. In this note we shall apply the same method to the interaction between two perfectly conducting plates.

Let us consider a cubic cavity of volume L^3 bounded by perfectly conducting walls and let a perfectly conducting square plate with side L be placed in this cavity parallel to the xy face and let us compare the situation in which this plate is at a small distance a from the xy face and the situation in which it is at a very large distance, say $L/2$. In both cases the expressions $\frac{1}{2}\Sigma \hbar\omega$ where the summation extends over all possible resonance frequencies of the cavities are divergent and devoid of physical meaning but the *difference* between these sums in the two situations, $\frac{1}{2}(\Sigma \hbar\omega)_I - \frac{1}{2}(\Sigma \hbar\omega)_{II}$, will be shown to have a well defined value and this value will be interpreted as the interaction between the plate and the xy face.

The possible vibrations of a cavity defined by

$$0 \leqslant x \leqslant L, \quad 0 \leqslant y \leqslant L, \quad 0 \leqslant z \leqslant a$$

have wave numbers

Quantum statistics

- **Microstate: Classical vs Quantum** (review of quantum mechanics)
  - ✓ Classical microstate could be described by accurate values of coordinates and conjugate momenta $\{\vec{p}_i, \vec{q}_i\}$.
  - ✓ In quantum mechanics, this is not doable: $\{\vec{p}_i, \vec{q}_i\}$ can not be determined simultaneously due the uncertainty principle.

  - ✓ The quantum microstate is specified by a *unit vector* $|\Psi\rangle$, which belongs to an infinite-dimensional *Hilbert space*. The vector $|\Psi\rangle$ can be written in terms of its components $\langle n|\Psi\rangle$ (probability amplitude), which are complex numbers, along a suitable set of orthonormal basis vectors $|n\rangle$ (quantum number n)

$|\Psi\rangle = \sum_n \langle n$ [redacted] $\rangle\, |n\rangle,$ $\langle \Psi$ [redacted] $\rangle \equiv \langle n$ [redacted] $\rangle^*,$ $\langle \Psi$ [redacted] $\rangle = \sum \langle \Psi$ [redacted] $\rangle \langle n$ [redacted] $\rangle = 1$

  - ✓ The square modulus $|\langle\Psi|n\rangle|^2$ is the probability that a measurement performed on the system will find it to have the quantum number n.

Quantum statistics

❑ Observables: Classical vs Quantum

- ✓ Classically, various observables are functions $\mathcal{O}\{\vec{p}_i, \vec{q}_i\}$

- ✓ In quantum mechanics, these functions are *Hermitian matrices* (operators).

- ✓ Unlike in classical mechanics, the value of an operator $\mathcal{O}$ is not uniquely determined for a particular microstate. It is instead a random variable, whose *quantum average* (Quantum expectation value) in a state $|\Psi\rangle$ is given by

$$\langle\mathcal{O}\rangle \equiv \langle\Psi|\mathcal{O}|\Psi\rangle \equiv \sum_{m,n}\langle\Psi\ \text{[redacted]}\rangle\langle m|\mathcal{O}|n\rangle\langle n\ \text{[redacted]}\rangle \qquad \sum_{n}|n\rangle\langle n| = 1$$

- ✓ To ensure that the quantum expectation value $\langle\mathcal{O}\rangle$ is real, the operators must be *Hermitian*, that is, satisfy

$$\mathcal{O}^{\dagger} = \mathcal{O}, \quad \text{where} \quad \left\langle m\middle|\mathcal{O}^{\dagger}\middle|n\right\rangle \equiv \langle n|\mathcal{O}|m\rangle^{*}.$$

Quantum statistics

❑ Macrostate: Classical vs Quantum

- ✓ **Classical:** We can form an *ensemble* of a large number N, of microstates μ_α $\{\vec{p}_i, \vec{q}_i\}$, corresponding to a given macrostate. The different microstates occur with probabilities p_α. Classical ***ensemble average***:

$$\overline{\mathcal{O}\left(\{\vec{p}_i,\vec{q}_i\}\right)} = \sum_\alpha p_\alpha \mathcal{O}\left(\mu_\alpha\right) = \int \prod_{i=1}^{N} \mathrm{d}^3\vec{p}_i\, \mathrm{d}^3\vec{q}_i\, \mathcal{O}\left(\{\vec{p}_i,\vec{q}_i\}\right)\rho\left(\{\vec{p}_i,\vec{q}_i\}\right)$$

$\rho\left(\{\vec{p}_i,\vec{q}_i\},t\right)$: Probability density

- ✓ **Quantum:** We can form an *ensemble* of a large number N, of microstates $|\Psi_\alpha\rangle$. The different microstates occur with probabilities p_α. ***Ensemble average of quantum expectation values*** **(*quantum average*):**

$$\overline{\langle\mathcal{O}\rangle} = \sum_\alpha p_\alpha \langle\Psi_\alpha|\mathcal{O}|\Psi_\alpha\rangle = \sum_{\alpha,m,n} p_\alpha \langle n|\Psi_\alpha\rangle\langle\Psi_\alpha|m\rangle\langle m|\mathcal{O}|n\rangle$$

$$= \sum_{m,n} \langle n|\rho|m\rangle\langle m|\mathcal{O}|n\rangle = \mathrm{tr}(\rho\mathcal{O})$$

Define the *density matrix* $\langle n|\rho(t)|m\rangle \equiv \sum_\alpha p_\alpha \langle n|\Psi_\alpha(t)\rangle\langle\Psi_\alpha(t)|m\rangle.$

Stripped of the choice of basis, the ***density matrix*** (operator) is

$$\rho(t) = \sum_\alpha p_\alpha |\Psi_\alpha(t)\rangle\langle\Psi_\alpha(t)|$$

Quantum statistics

The density matrix encodes the statistical state of a quantum system. Using it, we can describe quantum ensembles such as the microcanonical, canonical, and grand canonical ensembles. It's properties:

$$\rho(t)=\sum_{\alpha} p_{\alpha}\,|\Psi_{\alpha}(t)\rangle\langle\Psi_{\alpha}(t)|$$

☐ **Properties of the density matrix.**

(i) Normalization: $\mathrm{tr}(\rho)=?$

$$\mathrm{tr}(\rho)=\sum_{n}\langle n|\rho|n\rangle=\sum_{\alpha,n} p_{\alpha}\left|\langle n|\Psi_{\alpha}\rangle\right|^{2}=\sum_{\alpha} p_{\alpha}\left(\sum_{n}\left|\langle n|\Psi_{\alpha}\rangle\right|^{2}\right)=\sum_{\alpha} p_{\alpha}=1$$

(ii) Hermitian: ensures expectation values are real. $\rho^{\dagger}=\rho$

(iii) Positive: For any $|\Phi\rangle$,

$$\langle\Phi|\rho|\Phi\rangle=\sum_{\alpha} p_{\alpha}\langle\Phi|\Psi_{\alpha}\rangle\langle\Psi_{\alpha}|\Phi\rangle=\sum_{\alpha} p_{\alpha}\left|\langle\Phi|\Psi_{\alpha}\rangle\right|^{2}\geq 0$$

These three conditions guarantee that the density matrix behaves like a probability distribution in quantum mechanics.

Next, we will look at the several different ensembles.

Quantum statistics

- ☐ **Microcanonical ensemble:** Isolated system

Energy is fixed at E. All quantum states with energy E are equally probable.

Energy eigenstates: $\hat{\mathcal{H}}|n\rangle = \varepsilon_n |n\rangle$

Only eigenstates satisfying $\varepsilon_n = E$ are accessible

If there are $\Omega(E)$ states with energy E: $$p_n = \begin{cases} \dfrac{1}{\Omega(E)}, & \varepsilon_n = E \\ 0 & \varepsilon_n \neq E \end{cases}$$

Using the energy eigen basis, the density matrix becomes:

$$\rho(t) = \sum_\alpha p_\alpha |\Psi_\alpha(t)\rangle\langle\Psi_\alpha(t)| \qquad \Rightarrow \rho = \sum_n p_n |n\rangle\langle n| = \sum_n \frac{1}{\Omega(E)} |n\rangle\langle n|$$

We can see that in the energy eigen basis, the density matrix is diagonal. So we have:

$$\langle n|\rho|m\rangle = \begin{cases} \dfrac{1}{\Omega(E)}, & \varepsilon_n = E, \text{and } m = n, \\ 0 & \varepsilon_n \neq E, \text{or } m \neq n \end{cases}$$

Quantum statistics

- ☐ **Microcanonical ensemble:** Isolated system

$$\langle n|\rho|m\rangle = \begin{cases} \dfrac{1}{\Omega(E)}, & \varepsilon_n = E, \text{and } m = n, \\ 0 & \varepsilon_n \neq E, \text{or } m \neq n \end{cases}$$

All eigenstates with energy *E* have equal probability.

Equivalent to the classical assumption of equal a priori equilibrium probabilities.

$$\text{Normalization:} \quad \mathrm{tr}(\rho) = \sum_n \langle n|\rho|n\rangle = \sum_n \frac{1}{\Omega(E)} = \frac{1}{\Omega(E)} \sum_n = 1$$

$$\Omega(E) = \sum_n \delta\left(E - \varepsilon_n\right)$$: The number of eigenstates of *H* with energy *E*.

The microcanonical ensemble defines equilibrium, but in quantum systems counting all states with exactly the same energy is very hard, so we usually switch to the canonical ensemble for calculations.

Quantum statistics

- ☐ **Canonical ensemble.** A fixed temperature $T = 1/k_B\beta$ can be achieved by putting the system in contact with a reservoir. The partition function is

Energy eigenstates: $\hat{\mathcal{H}}|n\rangle = \varepsilon_n |n\rangle$ Boltzmann probability: $p_n = \dfrac{\exp(-\beta\varepsilon_n)}{Z}$

Using the energy eigen basis, the density matrix becomes:

$$\rho(t) = \sum_\alpha p_\alpha |\Psi_\alpha(t)\rangle\langle\Psi_\alpha(t)| \qquad \Rightarrow \rho = \sum_n p_n |n\rangle\langle n| = \sum_n \frac{\exp(-\beta\varepsilon_n)}{Z}|n\rangle\langle n|$$

$$\mathrm{tr}(\rho) = \sum_n \langle n|\rho|n\rangle = 1 = \sum_n \frac{\exp(-\beta\varepsilon_n)}{Z}$$

So, we get partition function: $Z = \sum_n \exp(-\beta\varepsilon_n)$

Since: $\sum_n \exp(-\beta\varepsilon_n) = \sum_n \langle n|\exp(-\beta\hat{H})|n\rangle$

We obtain the operator form of partition function: $Z = \mathrm{tr}\left[\exp(-\beta\hat{\mathcal{H}})\right]$

Quantum statistics

- ☐ **Grand canonical ensemble.**

The system can exchange energy and particles with a reservoir. The particle number N is therefore not fixed.

The chemical potential μ controls the average particle number.

Quantum microstates with indefinite particle number span a so-called *Fock space*.

Probability of a state: $p_{n,N} = \dfrac{\exp\left[-\beta(\varepsilon_{n,N} - \mu N\right]}{\mathcal{Q}}$

The corresponding partition function (operator form) is:

$$\mathcal{Q}(\beta,\mu) = \mathrm{tr}\left[\exp\left(-\beta\hat{\mathcal{H}} + \beta\mu N\right)\right] = \sum_{N=0}^{\infty} \mathrm{e}^{\beta\mu N} Z_N(\beta\hat{\mathcal{H}})$$

The grand canonical ensemble is similar to the canonical ensemble, except that the particle number can also fluctuate.

Quantum statistics

❑ **Ideal quantum gas: Canonical ensemble vs Grand canonical ensemble.**

We can compute the partition function Z_N in the **energy basis** as

$$Z_N = \mathrm{tr}\left[\exp\left(-\beta\hat{\mathcal{H}}\right)\right] = \sum_{\{\vec{k}_\alpha\}}^{\prime} \exp\left[-\beta\sum_{\alpha=1}^{N}\mathcal{E}\left(\vec{k}_\alpha\right)\right] = \sum_{\{n_{\vec{k}}\}}^{\prime}\exp\left[-\beta\sum_{\vec{k}}\mathcal{E}(\vec{k})n(\vec{k})\right]$$

The occupation numbers $\{n_{\vec{k}}\}$ are restricted to $\sum_{\vec{k}} n_{\vec{k}} = N$, and $n_{\vec{k}} = 0, 1, 2 \cdots$ for bosons, while $n_{\vec{k}} = 0$ or 1 for fermions.

These sums are difficult to perform due to the restrictions.

In the grand canonical ensemble the particle number can fluctuate, so the constraint $\sum_{\vec{k}} n_{\vec{k}} = N$ disappears.

Then, the first constraint can be removed by using the grand partition function,

$$\mathcal{Q}_\eta(T,\mu) = \sum_{N=0}^{\infty} \mathrm{e}^{\beta\mu N}\sum_{\{n_{\vec{k}}\}}^{\prime}\exp\left[-\beta\sum_{\vec{k}}\mathcal{E}(\vec{k})n_{\vec{k}}\right] = \prod_{\vec{k}}\sum_{\{n_{\vec{k}}\}}^{\eta}\exp\left[-\beta(\mathcal{E}(\vec{k})-\mu)n_{\vec{k}}\right]$$

The sums over $\{n_{\vec{k}}\}$ can now be performed independently for each $\vec{k}$, subject to the restrictions on occupation numbers imposed by particle symmetry.

Quantum statistics

- **Grand canonical ensemble.**

$$\mathcal{Q}_\eta(T,\mu) = \prod_{\vec{k}} \sum_{\{n_{\vec{k}}\}}^{\eta} \exp\left[-\beta(\mathcal{E}(\vec{k})-\mu)n_{\vec{k}}\right]$$

For ***fermions***, $n_{\vec{k}} = 0$ or 1, and

$$\mathcal{Q}_- = \prod_{\vec{k}} [1+\exp(\beta\mu-\beta\mathcal{E}(\vec{k}))]$$

For ***bosons***, $n_{\vec{k}} = 0, 1, 2 \cdots$,
and summing the geometric series gives

$$\mathcal{Q}_+ = \prod_{\vec{k}} [1-\exp(\beta\mu-\beta\mathcal{E}(\vec{k}))]^{-1}$$

lnZ: The results for both cases can be presented simultaneously as

$$\ln \mathcal{Q}_\eta = -\eta \sum_{\vec{k}} \ln[1-\eta\exp(\beta\mu-\beta\mathcal{E}(\vec{k}))]$$

with $\eta = -1$ for fermions,
and $\eta = +1$ for bosons

Probability: In the grand canonical formulation, different one-particle states are occupied independently, with a joint probability (for *n* particle number)

$$p_\eta(\{n(\vec{k})\}) = \frac{1}{\mathcal{Q}_\eta} \prod_{\vec{k}} \exp\left[-\beta(\mathcal{E}(\vec{k})-\mu)n_{\vec{k}}\right]$$

$$z = \exp(\beta\mu)$$

The **occupation number** of a state of energy $\mathcal{E}(\vec{k})$ is given by

$$\langle n_{\vec{k}} \rangle_\eta = -\frac{\partial \ln \mathcal{Q}_\eta}{\partial(\beta\mathcal{E}(\vec{k}))} = \frac{1}{z^{-1}e^{\beta\mathcal{E}(\vec{k})}-\eta}$$

Quantum statistics

- ❑ **Grand canonical formulation.**

The *occupation number* of a state of energy $\mathcal{E}(\vec{k})$ is given by

$$\langle n_{\vec{k}} \rangle_\eta = \frac{1}{z^{-1} e^{\beta \mathcal{E}(\vec{k})} - \eta}, \text{ with } z = \exp(\beta\mu) \qquad \ln \mathcal{Q}_\eta = -\eta \sum_{\vec{k}} \ln[1 - \eta \exp(\beta\mu - \beta\mathcal{E}(\vec{k}))]$$

The internal energy, equation of state, and particle number are then given by

$$\begin{cases} E_\eta = \sum_{\vec{k}} \mathcal{E}(\vec{k}) \langle n_{\vec{k}} \rangle_\eta = \sum_{\vec{k}} \dfrac{\mathcal{E}(\vec{k})}{z^{-1} e^{\beta\mathcal{E}(\vec{k})} - \eta} \\ \beta P_\eta = \dfrac{\ln \mathcal{Q}_\eta}{V} \\ N_\eta = \sum_{\vec{k}} \langle n_{\vec{k}} \rangle_\eta = \sum_{\vec{k}} \dfrac{1}{z^{-1} e^{\beta\mathcal{E}(\vec{k})} - \eta} \end{cases}$$

Related C_V et al.

Equation of state

$\mathcal{G} = -k_B T \ln \mathcal{Q} = E - TS - \mu N = -PV$,

so $k_B T \ln \mathcal{Q} = PV$, and $\beta P = \ln \mathcal{Q} / V$

Determines the chemical potential

However, we need to know the energy dispersion $\varepsilon(\vec{k})$ (Like Debye/Einstein model)

Quantum statistics

❑ Non-relativistic ideal gas

For a non-relativistic gas in three dimension, $\mathcal{E}(\vec{k}) = \hbar^2 k^2/2m$, and $\sum_{\vec{k}} \longrightarrow V\int d^3\vec{k}/(2\pi)^3$ the left equations reduce to

$$\left\{\begin{aligned} E_\eta &= \sum_{\vec{k}} \frac{\mathcal{E}(\vec{k})}{z^{-1}\mathrm{e}^{\beta\mathcal{E}(\vec{k})}-\eta} \\ \beta P_\eta &= \frac{\ln Q_\eta}{V} \\ N_\eta &= \sum_{\vec{k}} \frac{1}{z^{-1}\mathrm{e}^{\beta\mathcal{E}(\vec{k})}-\eta} \end{aligned}\right. \qquad \left\{\begin{aligned} \varepsilon_\eta &\equiv \frac{E_\eta}{V} = g\int \frac{\mathrm{d}^3\vec{k}}{(2\pi)^3}\,\frac{\hbar^2k^2}{2m}\,\frac{1}{z^{-1}\exp\left(\beta\hbar^2k^2/2m\right)-\eta}, \\ \beta P_\eta &= -\eta g\int \frac{\mathrm{d}^3\vec{k}}{(2\pi)^3}\ln\left[1-\eta z\exp\left(-\beta\hbar^2k^2/2m\right)\right] \quad, \\ n_\eta &\equiv \frac{N_\eta}{V} = g\int \frac{\mathrm{d}^3\vec{k}}{(2\pi)^3}\,\frac{1}{z^{-1}\exp\left(\beta\hbar^2k^2/2m\right)-\eta}. \end{aligned}\right.$$

The ‘g’ is for spin degeneracy. For a *spin s*, in the absence of a magnetic field, different spin states have the same energy, and a *spin degeneracy* factor, $g = 2s + 1$.

$$\left\langle n_{\vec{k}}\right\rangle_\eta = \frac{1}{z^{-1}\mathrm{e}^{\beta\mathcal{E}(\vec{k})}-\eta} \qquad z = \exp(\beta\mu) \qquad \ln Q_\eta = -\eta\sum_{\vec{k}}\ln[1-\eta\exp(\beta\mu-\beta\mathcal{E}(\vec{k}))]$$

Next, we need to change from the k space to $\mathcal{E}$ space: energy density of states

Quantum statistics

❑ **Density of states:** $\varepsilon_{\vec{k}} = \frac{\hbar^2 \vec{k}^2}{2m}$ $\vec{k} = \frac{2\pi}{L}(n_x, n_y, n_z)$

In the momentum space, periodic boundary conditions, the smallest momentums are $\Delta k_x = \frac{2\pi}{L_x}$, ($n_x = 1$), $\Delta k_y = \frac{2\pi}{L_y}$, ($n_y = 1$), $\Delta k_z = \frac{2\pi}{L_z}$, ($n_z = 1$),
where L_x, L_y and L_z are the lengths in *xyz* space and $L_x \times L_y \times L_z = V$

Then, the **momentum density of states** is $\rho(\vec{k}) = \frac{1}{\Delta k_x}\frac{1}{\Delta k_x}\frac{1}{\Delta k_x} = \frac{L_x}{2\pi}\frac{L_y}{2\pi}\frac{L_z}{2\pi} = \frac{V}{(2\pi)^3}$

In a small volume $d^3\vec{k}$, the number of states $\rho(\vec{k})d^3\vec{k} = \frac{V}{(2\pi)^3}d^3\vec{k} = \frac{V}{(2\pi)^3}4\pi k^2 dk$

Change to energy basis: $|k| = \sqrt{2m\varepsilon/\hbar^2}$, then d$k = (1/2\hbar)(2m)^{1/2}\ (\varepsilon)^{-1/2}d\varepsilon$,
$\rho(\vec{k})d^3\vec{k} = \frac{V}{(2\pi)^3}4\pi k^2 dk = \frac{V}{(2\pi)^3}4\pi(2m\varepsilon/\hbar^2)(1/2\hbar)(2m)^{1/2}\ (\varepsilon)^{-1/2}d\varepsilon = g(\varepsilon)d\varepsilon$,

Therefore, the **energy density of states** $g(\varepsilon) = \frac{V}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} \varepsilon^{1/2}$

Quantum statistics

- **Non-relativistic ideal gas**

$$g(\varepsilon)d\varepsilon = \frac{V}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\varepsilon^{1/2}d\varepsilon$$

$$\begin{cases} \varepsilon_\eta = g\int \frac{\mathrm{d}^3\vec{k}}{(2\pi)^3}\frac{\hbar^2k^2}{2m}\frac{1}{z^{-1}\exp\left(\beta\hbar^2k^2/2m\right)-\eta}, \\ \beta P_\eta = -\eta g\int \frac{\mathrm{d}^3\vec{k}}{(2\pi)^3}\ln\left[1-\eta z\exp\left(\frac{-\beta\hbar^2k^2}{2m}\right)\right], \\ n_\eta = g\int \frac{\mathrm{d}^3\vec{k}}{(2\pi)^3}\frac{1}{z^{-1}\exp\left(\beta\hbar^2k^2/2m\right)-\eta}. \end{cases}$$

$$\begin{cases} \varepsilon_\eta = \frac{g}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\int\varepsilon^{1/2}d\varepsilon\frac{\varepsilon}{z^{-1}\exp\left(\beta\varepsilon\right)-\eta}, \\ \beta P_\eta = \frac{-\eta g}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\int\varepsilon^{1/2}d\varepsilon\ln\left[1-\eta z\exp\left(-\beta\varepsilon\right)\right], \\ n_\eta = \frac{g}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\int\varepsilon^{1/2}d\varepsilon\frac{1}{z^{-1}\exp\left(\beta\varepsilon\right)-\eta}. \end{cases}$$

Set: $x = \frac{\beta\hbar^2k^2}{2m} = \beta\varepsilon$

use: $\lambda = \frac{h}{\sqrt{2\pi mk_BT}}$

$$\begin{cases} \beta\varepsilon_\eta = \frac{g}{\lambda^3}\frac{2}{\sqrt{\pi}}\int_0^\infty\frac{\mathrm{d}x x^{3/2}}{z^{-1}\mathrm{e}^x-\eta} \\ \beta P_\eta = -\eta\frac{g}{2\pi^2}\frac{4\pi^{3/2}}{\lambda^3}\int_0^\infty\mathrm{d}x x^{1/2}\ln\left(1-\eta z\mathrm{e}^{-x}\right) \\ \quad = \frac{g}{\lambda^3}\frac{4}{3\sqrt{\pi}}\int_0^\infty\frac{\mathrm{d}x x^{3/2}}{z^{-1}\mathrm{e}^x-\eta}, \\ n_\eta = \frac{g}{\lambda^3}\frac{2}{\sqrt{\pi}}\int_0^\infty\frac{\mathrm{d}x x^{1/2}}{z^{-1}\mathrm{e}^x-\eta}. \end{cases}$$

$\Leftarrow E = \int_0^\infty d\varepsilon g(\varepsilon)n(\varepsilon)\varepsilon$

$\rightarrow PV = \frac{2}{3}E$

Integration by parts

Black body radiation

$$P = P_0 + \frac{1}{3}\frac{E}{V}.$$

Quantum statistics

- **Relativistic gas** $\varepsilon = cp = c\hbar k$

Density of state: $|k| = \varepsilon/c\hbar$, then $\mathrm{d}k = (1/c\hbar)d\varepsilon$, and $d^3\vec{k} = 4\pi k^2 dk = 4\pi(\varepsilon)^2(1/c\hbar)^3 d\varepsilon$

$\rho(\vec{k})d^3\vec{k} = \frac{V}{(2\pi)^3}d^3\vec{k} = \frac{V}{(2\pi)^3}4\pi(\varepsilon)^2(1/c\hbar)^3 d\varepsilon = g(\varepsilon)d\varepsilon,$ so $g(\varepsilon) = \frac{V}{2\pi^2}(c\hbar)^{-3}\varepsilon^2$

$$\begin{cases} \varepsilon_\eta = g\int \frac{\mathrm{d}^3\vec{k}}{(2\pi)^3}\frac{c\hbar k}{z^{-1}\exp(\beta c\hbar k)-\eta}, \\ \beta P_\eta = -\eta g\int \frac{\mathrm{d}^3\vec{k}}{(2\pi)^3}\ln\left[1-\eta z\exp(-\beta c\hbar k)\right], \\ n_\eta = g\int \frac{\mathrm{d}^3\vec{k}}{(2\pi)^3}\frac{1}{z^{-1}\exp(\beta c\hbar k)-\eta}. \end{cases}
\qquad
\begin{cases} \varepsilon_\eta = \frac{g}{2\pi^2(c\hbar)^3}\int \varepsilon^2\mathrm{d}\varepsilon\frac{\varepsilon}{z^{-1}\exp(\beta\varepsilon)-\eta}, \\ \beta P_\eta = \frac{-\eta g}{2\pi^2(c\hbar)^3}\int \varepsilon^2\mathrm{d}\varepsilon\ln\left[1-\eta z\exp(-\beta\varepsilon)\right], \\ n_\eta = \frac{g}{2\pi^2(c\hbar)^3}\int \varepsilon^2\mathrm{d}\varepsilon\frac{1}{z^{-1}\exp(\beta\varepsilon)-\eta}. \end{cases}$$

Set $x = \beta\varepsilon$,

$$\begin{cases} \beta\varepsilon_\eta = \frac{g}{2\pi^2}\left(\frac{k_BT}{c\hbar}\right)^3\int_0^\infty\frac{\mathrm{d}x x^3}{z^{-1}\mathrm{e}^x-\eta}, \longrightarrow P = \frac{1}{3}\frac{E}{V}. \\ \beta P_\eta = \frac{-\eta g}{2\pi^2}\left(\frac{k_BT}{c\hbar}\right)^3\int_0^\infty \mathrm{d}x x^2\ln\left(1-\eta z\mathrm{e}^{-x}\right) = \frac{\eta g}{6\pi^2}\left(\frac{k_BT}{c\hbar}\right)^3\int_0^\infty\frac{\mathrm{d}x x^3}{z^{-1}\mathrm{e}^x-\eta}, \\ n_\eta = \frac{g}{2\pi^2}\left(\frac{k_BT}{c\hbar}\right)^3\int_0^\infty\frac{\mathrm{d}x x^2}{z^{-1}\mathrm{e}^x-\eta}. \end{cases}$$

Integration by parts

Quantum statistics

- **Ideal quantum gas**

Relativistic gas:

$$\begin{cases} \beta\varepsilon_\eta = \dfrac{g}{2\pi^2}\left(\dfrac{k_BT}{c\hbar}\right)^3 \displaystyle\int_0^\infty \dfrac{\mathrm{d}x x^3}{z^{-1}\mathrm{e}^x-\eta}, \\ \beta P_\eta = \eta \dfrac{g}{6\pi^2}\left(\dfrac{k_BT}{c\hbar}\right)^3 \displaystyle\int_0^\infty \dfrac{\mathrm{d}x x^3}{z^{-1}\mathrm{e}^x-\eta} \\ n_\eta = \dfrac{g}{2\pi^2}\left(\dfrac{k_BT}{c\hbar}\right)^3 \displaystyle\int_0^\infty \dfrac{\mathrm{d}x x^2}{z^{-1}\mathrm{e}^x-\eta}. \end{cases}, \quad \begin{cases} \varepsilon_\eta = 3P_\eta, \\ \beta P_\eta = \dfrac{g}{\lambda^3} f_4^\eta(z), \\ n_\eta = \dfrac{g}{\lambda^3} f_3^\eta(z). \end{cases}$$

Non-relativistic gas:

$$\begin{cases} \beta\varepsilon_\eta = \dfrac{g}{\lambda^3}\dfrac{2}{\sqrt{\pi}} \displaystyle\int_0^\infty \dfrac{\mathrm{d}x x^{3/2}}{z^{-1}\mathrm{e}^x-\eta}, \\ \beta P_\eta = \dfrac{g}{\lambda^3}\dfrac{4}{3\sqrt{\pi}} \displaystyle\int_0^\infty \dfrac{\mathrm{d}x x^{3/2}}{z^{-1}\mathrm{e}^x-\eta} \\ n_\eta = \dfrac{g}{\lambda^3}\dfrac{2}{\sqrt{\pi}} \displaystyle\int_0^\infty \dfrac{\mathrm{d}x x^{1/2}}{z^{-1}\mathrm{e}^x-\eta}. \end{cases}, \quad \begin{cases} \varepsilon_\eta = \dfrac{3}{2} P_\eta, \\ \beta P_\eta = \dfrac{g}{\lambda^3} f_{5/2}^\eta(z), \\ n_\eta = \dfrac{g}{\lambda^3} f_{3/2}^\eta(z). \end{cases}$$

All have the general form: $f_m^\eta(z) = \dfrac{1}{(m-1)!}\displaystyle\int_0^\infty \dfrac{\mathrm{d}x x^{m-1}}{z^{-1}\mathrm{e}^x-\eta}$

$(1/2)! = \sqrt{\pi}/2,$
$(3/2)! = (3/2)\sqrt{\pi}/2.$

For non-integer, $m! \equiv \Gamma(m+1)$ is defined by the integral $\int_0^\infty dx x^m e^{-x}$.

These results describe the ideal gases as a function of z (**fugacity**): $\exp(\beta\mu)$

To find the $P_\eta(T)$ explicitly requires solving z from $n_\eta(z)$, i.e., find out $z(n_\eta)$.

To this end, we need to understand the behavior of the functions $f_m^\eta(z)$.

Quantum statistics: Discussion

- **Non-relativistic gas: high temperature, low density limit**

The high-temperature, low-density (non-degenerate) limit will be examined first.

Questions:

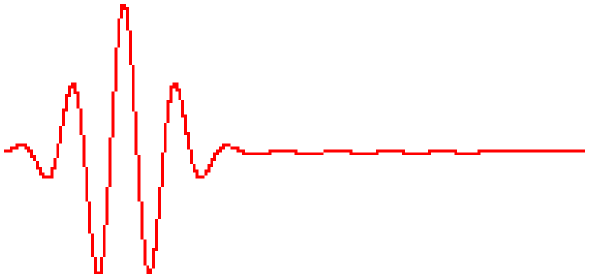
[1] In this limit, sign of μ? Value of $\exp[\beta(\mu\text{-}\varepsilon)]$?

[2] What is the physical meaning of “non-degenerate” at high temperature or low density?

[3] Can you guess the equation of state (βP_η) and energy (ε_η) at high temperature or low density?

$$\begin{cases} \beta P_\eta = \dfrac{g}{\lambda^3} f^{\eta}_{5/2}(z) = \dfrac{g}{\lambda^3}\dfrac{4}{3\sqrt{\pi}}\displaystyle\int_0^\infty \frac{\mathrm{d}x x^{3/2}}{z^{-1}\mathrm{e}^x-\eta}, \\ n_\eta = \dfrac{g}{\lambda^3} f^{\eta}_{3/2}(z) = \dfrac{g}{\lambda^3}\dfrac{2}{\sqrt{\pi}}\displaystyle\int_0^\infty \frac{\mathrm{d}x x^{1/2}}{z^{-1}\mathrm{e}^x-\eta}, \\ \beta\varepsilon_\eta = \dfrac{3}{2}\beta P_\eta = \dfrac{g}{\lambda^3}\dfrac{2}{\sqrt{\pi}}\displaystyle\int_0^\infty \frac{\mathrm{d}x x^{3/2}}{z^{-1}\mathrm{e}^x-\eta} \end{cases}$$

$$\lambda = \frac{h}{\sqrt{2\pi m k_B T}}$$



Quantum statistics

- ☐ **Non-relativistic gas: high temperature, low density limit**

$$x = \beta\varepsilon$$

$$z = \exp(\beta\mu)$$

$$f_m^\eta(z) = \frac{1}{(m-1)!}\int_0^\infty \frac{\mathrm{d}x x^{m-1}}{z^{-1}\mathrm{e}^x - \eta} = \frac{1}{(m-1)!}\int_0^\infty \mathrm{d}x x^{m-1}\left(z\mathrm{e}^{-x}\right)\left(1-\eta z\mathrm{e}^{-x}\right)^{-1}$$

$$= \frac{1}{(m-1)!}\int_0^\infty \mathrm{d}x x^{m-1}\sum_{\alpha=1}^\infty \left(z\mathrm{e}^{-x}\right)^\alpha \eta^{\alpha+1}$$

At high T, $\mu<0$, $\varepsilon>0$, so $ze^{-x} = e^{\beta(\mu-\varepsilon)} < 1$

$$\frac{1}{1-\eta z\mathrm{e}^{-x}} = \sum_{n=0}^\infty \left(\eta z\mathrm{e}^{-x}\right)^n$$

$$= \sum_{\alpha=1}^\infty \eta^{\alpha+1} z^\alpha \frac{1}{(m-1)!}\int_0^\infty \mathrm{d}x x^{m-1}\mathrm{e}^{-\alpha x}$$

$$\int_0^\infty dx x^n e^{-ax} = \frac{n!}{a^{n+1}}$$

$$= \sum_{\alpha=1}^\infty \eta^{\alpha+1}\frac{z^\alpha}{\alpha^m} = z + \eta\frac{z^2}{2^m} + \frac{z^3}{3^m} + \eta\frac{z^4}{4^m} + \cdots$$

$$\begin{cases} \dfrac{\beta P_\eta \lambda^3}{g} = f_{5/2}^\eta(z) = z + \eta\dfrac{z^2}{2^{5/2}} + \dfrac{z^3}{3^{5/2}} + \eta\dfrac{z^4}{4^{5/2}} + \cdots \\ \dfrac{n_\eta \lambda^3}{g} = f_{3/2}^\eta(z) = z + \eta\dfrac{z^2}{2^{3/2}} + \dfrac{z^3}{3^{3/2}} + \eta\dfrac{z^4}{4^{3/2}} + \cdots \end{cases}$$

Insert $z(n=N/V)$ to find out $P(V, N, T)$

$z = \mathrm{e}^{(\beta\mu)}$ is determined by density n

solve z to find out $z(n=N/V)$

Quantum statistics

- ❑ **Non-relativistic gas: high temperature, low density limit**

$$\frac{n_\eta \lambda^3}{g} = z + \eta \frac{z^2}{2^{3/2}} + \frac{z^3}{3^{3/2}} + \eta \frac{z^4}{4^{3/2}} + \cdots \rightarrow z = \frac{n_\eta \lambda^3}{g} - \eta \frac{z^2}{2^{3/2}} - \frac{z^3}{3^{3/2}} - \eta \frac{z^4}{4^{3/2}} + \cdots$$

The z can be solved **perturbatively**, by the **recursive procedure** of substituting the solution up to a lower order, as

1st order: $z = \frac{n_\eta \lambda^3}{g} - \eta \frac{z^2}{2^{3/2}} - \frac{z^3}{3^{3/2}} - \cdots = \left(\frac{n_\eta \lambda^3}{g}\right) - \frac{\eta}{2^{3/2}} \left(\frac{n_\eta \lambda^3}{g}\right)^2 - \cdots$ plug in 0th order $z = \frac{n_\eta \lambda^3}{g}$

2nd order: $z = \frac{n_\eta \lambda^3}{g} - \eta \frac{z^2}{2^{3/2}} - \frac{z^3}{3^{3/2}} - \cdots$ plug in 1st order $z = \left(\frac{n_\eta \lambda^3}{g}\right) - \frac{\eta}{2^{3/2}} \left(\frac{n_\eta \lambda^3}{g}\right)^2$

$$= \left(\frac{n_\eta \lambda^3}{g}\right) - \frac{\eta}{2^{3/2}} \left(\frac{n_\eta \lambda^3}{g}\right)^2 + \left(\frac{1}{4} - \frac{1}{3^{3/2}}\right) \left(\frac{n_\eta \lambda^3}{g}\right)^3 - \cdots.$$ (Your homework)

Substituting the 2nd order: $\frac{\beta P_\eta \lambda^3}{g} = z + \eta \frac{z^2}{2^{5/2}} + \frac{z^3}{3^{5/2}} + \eta \frac{z^4}{4^{5/2}} + \cdots$ (Your homework)

$$\frac{\beta P_\eta \lambda^3}{g} = \left(\frac{n_\eta \lambda^3}{g}\right) - \frac{\eta}{2^{3/2}} \left(\frac{n_\eta \lambda^3}{g}\right)^2 + \left(\frac{1}{4} - \frac{1}{3^{3/2}}\right) \left(\frac{n_\eta \lambda^3}{g}\right)^3 + \frac{\eta}{2^{5/2}} \left(\frac{n_\eta \lambda^3}{g}\right)^2 - \frac{1}{8} \left(\frac{n_\eta \lambda^3}{g}\right)^3 + \frac{1}{3^{5/2}} \left(\frac{n_\eta \lambda^3}{g}\right)^3 + \cdots$$

Quantum statistics: Discussion

- ☐ **Non-relativistic gas: high temperature, low density limit**

$$\frac{\beta P_\eta \lambda^3}{g} = \left(\frac{n_\eta \lambda^3}{g}\right) - \frac{\eta}{2^{3/2}}\left(\frac{n_\eta \lambda^3}{g}\right)^2 + \left(\frac{1}{4} - \frac{1}{3^{3/2}}\right)\left(\frac{n_\eta \lambda^3}{g}\right)^3 + \frac{\eta}{2^{5/2}}\left(\frac{n_\eta \lambda^3}{g}\right)^2 - \frac{1}{8}\left(\frac{n_\eta \lambda^3}{g}\right)^3 + \frac{1}{3^{5/2}}\left(\frac{n_\eta \lambda^3}{g}\right)^3 + \cdots$$

Question: How can we understand this equation of state (ideal quantum gas)?

The pressure of quantum gas can thus be expressed in the form of

$$P_\eta = n_\eta k_B T\left[1 - \frac{\eta}{2^{5/2}}\left(\frac{n_\eta \lambda^3}{g}\right) + \left(\frac{1}{8} - \frac{2}{3^{5/2}}\right)\left(\frac{n_\eta \lambda^3}{g}\right)^2 + \cdots\right]$$

$$\beta P = \frac{N}{V}\left[1 + B_2(T)\frac{N}{V} + B_3(T)\left(\frac{N}{V}\right)^2 + \cdots\right].$$

The pressure of ideal quantum gas can be expressed in the form of virial expansion!
The second virial coefficient $B_2 = -\eta\lambda^3/(2^{5/2}g)$ for $g = 1$. Not zero!

Next week

Fermi gas