Quantum statistical mechanics: Introduction

0.0.1 Microstates
Let $H$ be the Hamiltonian of the system we wish to study:

$$H = \sum_{i=1}^{N} \frac{p_i^2}{2m_i} + V(\{q_i\}),$$

(0.0.1)

where $p_i$ is the momentum of the $i$th particle, $q_i$ its position and $V$ the potential energy.

Let $\epsilon$ be the eigenvalues of $H$:

$$H|\epsilon\rangle = \epsilon|\epsilon\rangle.$$  

(0.0.2)

Since a quantum-mechanical state corresponds to a ray of an eigenvector, the normalized eigenket $|\epsilon\rangle$ is understood as a microstate.

0.0.2 Microcanonical ensemble
The totality $\tilde{\omega}(E)$ for a macroscopically small leeway $\Delta E$ of microstates corresponding to a thermodynamics state (specified by the thermodynamic coordinates) is called the microcanonical ensemble, which is a vector space spanned by $|\epsilon\rangle$s compatible with the macrostate.

Remark If a macrostate is specified by the thermodynamic coordinates $\{E, X\}$ and if the operators corresponding to the coordinates are not commutative, how to choose the compatible microstates still has delicate issues.

0.0.3 Microcanonical partition function
The number $\omega(E)$ of microstates in $\tilde{\omega}(E)$ is the microcanonical partition function. Since rays correspond to individual microstates, the dimension of $\tilde{\omega}$ is $\omega(E)$. Let the resolution of unity for $\tilde{\omega}(E)$ be

$$1 = \sum_{|\epsilon\rangle \in \tilde{\omega}} |\epsilon\rangle\langle \epsilon|.$$  

(0.0.3)

Then, the microcanonical partition function reads

$$w(E) = \text{Tr } 1 = \text{dim } \tilde{\omega}(E).$$  

(0.0.4)

0.0.4 Statistical calculation in quantum mechanics
Let $O$ be an observable. That is $O$ is a self-adjoint operator. Then, for a microstate $|a\rangle$ what we observe is

$$\langle a|O|a\rangle = \text{Tr } |a\rangle\langle a|O.$$  

(0.0.5)

Therefore, if we encounter state $|a\rangle$ with probability $p_a$, then the overall average can be written as

$$\langle O \rangle = \sum_a p_a \langle a|O|a\rangle = \text{Tr } \sum_a |a\rangle p_a \langle a|O.$$  

(0.0.6)

\footnote{1}Precisely speaking, say, the energy is in $(E - \Delta E, E]$.  

\footnote{2}Recall $\text{Tr } AB = \text{Tr } BA$.}
Notice that $|a\rangle\langle a|$ is the projection\(^3\) onto state $|a\rangle$. Therefore, if we introduce

$$\rho = \sum_a |a\rangle p_a \langle a|,$$

we may write

$$\langle O \rangle = Tr \rho O.$$  \(0.0.8\)

$\rho$ is an example of the density operator.

### 0.0.5 Density operator

Quantum mechanically, the expectation value of an observable $O$ over a certain set of states with a statistical law is generally expressed with the aid of the density operator $\rho$ as

$$\langle O \rangle = Tr (\rho O).$$  \(0.0.9\)

The density operator, which is a counterpart of the density distribution function in the ordinary statistics, is a self-adjoint operator satisfying the following two conditions:

(i) normalization condition: $Tr \rho = 1$.

(ii) positivity: for any positive definite operator\(^4\) $A$, $Tr(\rho A) \geq 0$.

The probability $P(A)$ for a subspace $A$ of the microstate space ($A$ may be understood as a quantum event) is expressed as

$$P(A) = Tr(\rho P_A),$$  \(0.0.10\)

where $P_A$ is the projection onto the subspace $A$ as shown in the footnote.\(^5\)

### 0.0.6 Pure state and mixed state

A state we can observe by a single observation is always a state described by a single ket. If all the observations can observe identical quantum state (ket), the density operator describing the state reads $\rho = |a\rangle\langle a|$, and the state is called a pure state. In this case

$$\rho^2 = \rho.$$  \(0.0.12\)

\(^3\) Projection operator: If an operator $P$ satisfies $P^2 = P$, $P$ is called a projection. Especially if $P = P^*$, it is called an orthogonal projection.

\(^4\) Positive definite operator: An operator $A$ is positive definite, if $\langle*|A|*\rangle \geq 0$ for any non-zero ket $|*\rangle$. If $A$ is an observable (i.e., self-adjoint), this means that all the eigenvalues of $A$ are nonnegative.

\(^5\) Let the subspace $A$ be spanned by an orthonormal set $\{|a\rangle\}$: $P_A = \sum_a |a\rangle\langle a|$. Notice that $\rho$ is self-adjoint, so it has an ON-basis $\{|e_i\rangle\}$ to diagonalize it as $\rho = \sum_i |e_i\rangle p_i \langle e_i|$, where $\sum p_i = 1$ with $p_i \geq 0$ thanks to (i) and (ii) above.

$$Tr(\rho P_A) = Tr \left[ \left( \sum_i |e_i\rangle p_i \langle e_i| \right) \left( \sum_a |a\rangle\langle a| \right) \right] = \sum_i p_i \langle e_i| \left( \sum_a |a\rangle\langle a| \right) |e_i\rangle.$$  \(0.0.11\)

Notice that $|\langle e_i|a\rangle|^2$ may be interpreted as the probability that the state $|a\rangle$ is observed when the actual state is $|e_i\rangle$ (cf. Born). Then, $p_a = \sum_i p_i |\langle e_i|a\rangle|^2$ is the probability to encounter the state $a$, if the statistical property of the system is described by $\rho$. Therefore, \(0.0.11\) implies $Tr(\rho P_A) = \sum_{a \in A} p_a$, which is indeed the probability to observe an event $A$. 
That is, the density operator is a projection.

Otherwise, we say the state described by the density operator is a mixed state. In this case, the density operator describes the outcome of observations on a system that is not described by a single quantum state (single ket). \((0.0.7)\) is an example, if at least one of \(p_a \in (0, 1)\).

0.0.7 Microcanonical density operator
If we assume the principle of equal probability, any state in a microcanonical ensemble of a system is equally probable (formally with probability \(1/w(E)\) \(^6\)). Therefore, the microcanonical density operator for the energy shell \((E - \Delta E, E]\) may be written as

\[
\rho = \sum_\epsilon |\epsilon\rangle \frac{\chi_{\Delta E}(\epsilon)}{w(E)} \langle \epsilon|,
\]

(0.0.13)

where \(\chi_{\Delta E}\) is the indicator of \((E - \Delta E, E]\). The summation is over all the eigenvalues of the system Hamiltonian.

0.0.8 Canonical density operator
Define for a Hamiltonian \(\hat{H}\)

\[
\rho = \frac{1}{Z} e^{-\beta \hat{H}},
\]

(0.0.14)

where \(Z = \text{Tr} e^{-\beta \hat{H}}\) is the canonical partition function. Then,

\[
\text{Tr} (\rho P_E) = \frac{1}{Z} w(E) e^{-\beta E},
\]

(0.0.15)

where \(P_E\) is the projection onto \(\tilde{w}(E)\), the totality of the energy eigenstates of the Hamiltonian \(H\) belonging to \((E - \Delta E, E]\).

If we assume the principle of equal probability, the probability for the system to have energy \(E\) is proportional to \(w(E) w_{\text{II}}(E_0 - E) \propto w(E) e^{-\beta E}\). Therefore, (0.0.15) is the correct probability to find microstates with energy around \(E\), so (0.0.14) is the correct density operator for a canonical ensemble consistent with the principle of equal probability.

0.0.9 Classical ideal gas and de Broglie wavelength
The classical ideal gas is characterized by the total absence of quantum effect: here, quantum effect means that the particles can delocalize. Consider a gas consisting of \(N\) identical noninteracting particles. To ignore all quantum effects, the average de Broglie wavelength of each particle must be much smaller than the average interparticle distance. The de Broglie wavelength \(\lambda\) may be estimated as

\[
\lambda \sim \frac{\hbar}{\sqrt{mk_B T}},
\]

(0.0.16)

\(^6\)Here, for simplicity, work coordinates are suppressed. It is always easy to include them classically, and quantum mechanically if the observables corresponding to the densities are commutative. Otherwise, it is not easy as noted in the construction of the microcanonical ensemble.
where \( m \) is the mass of the particle, and \( h \) is Planck’s constant. This estimate is due to 
\[
\lambda = \frac{h}{p} = \frac{h}{\sqrt{2mK}} \quad \text{and} \quad K \sim k_B T,
\]
where \( p \) is the representative value of the magnitude of the momentum of a particle, and \( K \) is the representative value of the one-particle kinetic energy. The mean particle distance is \( \sqrt{V/N} \), so the condition we want is 
\[
\sqrt{V/N} \gg \lambda,
\]
or
\[
\frac{N}{V} \ll \left( \frac{mk_B T}{h^2} \right)^{3/2}.
\] (0.0.17)

When this inequality is satisfied, we say the gas is classical.\(^7\)

Since there are no interactions among particles, each particle cannot sense the density. Consequently, the internal energy of the system must be a function of \( T \) only: \( E = E(T) \). This is a good characterization of ideal gases.

**0.0.10 Single particle states**

Let us first compute the number of microscopic states allowed to a single particle in a box of volume \( V \). To this end we solve the Schrödinger equation in a cube with edges of length \( L \):
\[
-\frac{\hbar^2}{2m} \Delta \psi = E \psi; \tag{0.0.18}
\]
\( \Delta \) is the Laplacian, and a homogeneous Dirichlet boundary condition \( \psi = 0 \) at the wall is imposed. As is well-known, the eigenfunctions are:
\[
\psi_k \propto \sin k_x x \sin k_y y \sin k_z z \tag{0.0.19}
\]
with the following quantization condition due to the boundary condition:
\[
k \equiv (k_x, k_y, k_z) = \frac{\pi}{L} (n_x, n_y, n_z) \equiv \frac{\pi}{L} n.
\] (0.0.20)
Here, \( n_x, \cdots \) are positive integers, \( 1, 2, \cdots \). The eigenfunction \( \psi_k \) belongs to the eigenvalue (energy) \( \hbar^2 k^2 / 2m \).

The number of states with wave number vectors \( k \) in the range \( k \) to \( k + dk \) is
\[
\# \{k \mid k < |k| < k + dk\} = \# \left\{ n \left| \frac{L}{\pi} k < |n| < \frac{L}{\pi} (k + dk) \right. \right\}
\]
\[
= \left( \frac{1}{8} 4\pi n^2 dn = \right) \frac{1}{8} \frac{L^3}{\pi^3} 4\pi k^2 dk = \frac{1}{2\pi^2} V k^2 dk.
\] (0.0.21)

The factor 1/8 is required because the relevant \( k \) are only in the first octant (all the components must be positive).

\(^7\)Notice that the dynamics of internal degrees of freedom such as vibration and rotation need not be classical as we will see in Section 23.
0.0.11 Classical ideal gas: single particle canonical partition function

Now we can compute the canonical partition function for a single particle using its definition:

\[
Z_1 = \sum_{n_x>0, n_y>0, n_z>0} \exp(-\beta E)
\]

(0.0.22)

\[
= \int \# \left\{ \mathbf{n} \mid \frac{L}{\pi} k < |\mathbf{n}| < \frac{L}{\pi} (k + dk) \right\} \exp(-\beta k^2 \hbar^2/2m)
\]

(0.0.23)

\[
\approx \frac{1}{8 \pi^3} \int_0^\infty 4\pi k^2 dk \exp(-\beta k^2 \hbar^2/2m).
\]

(0.0.24)

The integration is readily performed. (0.0.24) is

\[
Z_1(V) = \frac{1}{N!} Z_N
\]

(0.0.25)

and we know

\[
\int_{-\infty}^\infty dx e^{-ax^2} = \sqrt{\frac{\pi}{a}}.
\]

(0.0.26)

Therefore,

\[
Z_1(V) = V \frac{1}{8 \pi^3} \left( \frac{2\pi m k_B T}{\hbar^2} \right)^{3/2} = V \left( \frac{1}{4\pi^2} \right)^{3/2} \left( \frac{8\pi^3 m k_B T}{\hbar^2} \right)^{3/2}.
\]

(0.0.27)

That is,

\[
Z_1(V) = V \left( \frac{2\pi m k_B T}{\hbar^2} \right)^{3/2}.
\]

(0.0.28)

The important point of this result is that \(Z_1 \propto V\).

0.0.12 Classical ideal gas canonical partition function

Since the particles in a pure ideal gas are indistinguishable canonical partition function in terms of the phase integral reads the total canonical partition function should read

\[
Z = \frac{1}{N!} Z_N^N.
\]

(0.0.29)

Therefore, the canonical partition function for a classical ideal gas reads

\[
Z_{\text{ideal}} = \frac{V^N}{N!} \left( \frac{2\pi m k_B T}{\hbar^2} \right)^{3N/2} = \left[ \frac{V e}{N} \left( \frac{2\pi m k_B T}{\hbar^2} \right)^{3/2} \right]^N.
\]

(0.0.30)

Notice that \(h^{N_0}\) naturally appears.
0.0.13 Ideal gas with internal degrees of freedom

If an ideal gas particle has internal degrees of freedom, the Hamiltonian of the gas consists of two parts:

\[ H = H_0 + H_i, \tag{0.0.31} \]

where \( H_0 \) is the Hamiltonian of the translational motion

\[ H_0 = \sum_{i=1}^{N} \frac{1}{2m} p_i^2, \tag{0.0.32} \]

and \( H_i \) is the Hamiltonian governing the internal degrees of freedom, which is a sum of Hamiltonians \( h_i \) governing individual molecular internal motions:

\[ H_i = \sum_{i=1}^{N} h_i. \tag{0.0.33} \]

The translational degrees and internal degrees of freedom are not interacting, so they are completely independent (mechanically and statistically). Hence, the canonical partition function reads

\[ Z = Z_{\text{ideal}} Z_i, \tag{0.0.34} \]

where \( Z_{\text{ideal}} \) is the partition function for a monatomic ideal gas we computed before, and \( Z_i \) is the “internal” partition function

\[ Z_i = z^N, \tag{0.0.35} \]

with

\[ z = \sum e^{-\beta h} = \text{Tr} e^{-\beta h}. \tag{0.0.36} \]

Here, the suffix to denote a particular molecule has been dropped, since all the internal partition functions are identical for identical molecules.

0.0.14 Collection of harmonic oscillators: classical approach

An important internal motion of gas molecules is vibration. Let us consider a diatomic molecule whose vibrational degree of freedom may be described as a 1D harmonic oscillator of (effective mass) \( m \) and angular frequency \( \omega \):

\[ h = \frac{1}{2m} (p^2 + m^2 \omega^2 q^2). \tag{0.0.37} \]

Although we already know that this oscillator should not be treated classically, let us study it classically to know how bad the result is:

\[ z = \frac{1}{\hbar} \int dp dq e^{-\beta(p^2 + m^2 \omega^2 q^2)/2m} = \frac{1}{\hbar} \left( \frac{2\pi m}{\beta} \frac{2\pi}{m\omega^2} \right)^{1/2} \frac{k_B T}{\hbar \omega}. \tag{0.0.38} \]

Notice that \( z \propto k_B T \hbar \omega \) is dimensional-analytically obvious. Therefore,

\[ Z_i = \left( \frac{k_B T}{\hbar \omega} \right)^N = (\beta \hbar \omega)^{-N}. \tag{0.0.39} \]
0.0.15 Einstein model: classical
At this juncture, we must realize that the partition function $Z_i$ is also the canonical partition function of a collection of 1D oscillators sitting individually at lattice points.

The internal energy of a collection of $N$ 1D oscillators is

$$E = N \frac{\partial}{\partial \beta} \log(\beta \hbar \omega) = N / \beta = N k_B T. \quad (0.0.40)$$

Therefore,

$$S = \frac{E - A}{T} = N k_B + N k_B \log(k_B T / \hbar \omega) = N k_B \log T + \text{const.} \quad (0.0.41)$$

You should realize that (0.0.40) is the outcome of the equipartition of energy: $\langle m v^2 / 2 \rangle = k_B T / 2$ and you know the average kinetic and potential energies of a harmonic oscillators are identical.

0.0.16 Fundamental difficulty of classical harmonic oscillator
The result (0.0.41) implies that in the $T \searrow 0$ limit $S \searrow -\infty$. Therefore, to describe a harmonic oscillator at $T$ knowing only the state information at much lower temperature $T_0$ a large amount of additional information $\sim \log(T/T_0)$ is required, especially if $T_0$ is close to zero.

This must violate a certain fundamental principle: the finiteness principle that a finite object with finite energy should require only a finite amount of information for its complete description (if totally isolated).\(^8\)

This is a good occasion to discuss another principle of thermodynamics: the third law.

0.0.17 The third law of thermodynamics
Nernst empirically found that all the entropy changes asymptotically vanish in the $T \to 0$ limit. In particular, all the derivatives of entropy $S$ vanish as $T \to 0$ (Nernst’s law). All the specific heat vanishes as $T \to 0$. Nernst concluded that entropy becomes constant (independent of any thermodynamic variables) in the $T \to 0$ limit. Later, Planck chose this constant to be zero (the concept of absolute entropy).

We adopt the following as the third law of thermodynamics:

Reversible change of entropy $\Delta S$ vanishes in the $T \to 0$ limit.

This implies that to describe the state of a macroscopic system at $T = 0$, required information is subextensive, or the number of YES-NO questions needed to know the macrostate is zero per particle.

The entropy we computed classically above must be wrong.

\(^8\) (Consequence of the finiteness principle) If we combine Boltzmann’s principle and this finiteness principle, then Boltzmann’s principle must not be applicable to an extremely small phase volumes. That is there must be ‘information quantum’ that has the dimension of $(\text{action})^3 N$. Thus, notice that the existence of a fundamental quantity with the dimension of action (something like $\hbar$) is required by the finiteness principle and thermodynamics.
0.0.18 3D crystal; classical treatment
Consider a crystal made of $N$ atoms, having $3N$ mechanical degrees of freedom. Small displacements of atoms around their mechanical equilibrium positions should be a kind of harmonic oscillation. Thus, we may regard the crystal as a set of $3N$ independent harmonic oscillators (modes) of various frequencies (due to coupling among atoms). The canonical partition function of the total system is the product of the canonical partition function for each harmonic mode.

Treating the system completely classically and using the definition of the classical partition function (0.0.38), the partition function reads

$$Z = \prod_{i=1}^{3N} \frac{k_B T}{\hbar \omega_i}. \quad (0.0.42)$$

The contribution of these oscillators to the internal energy is readily obtained from the equipartition of energy as

$$E = 3Nk_B T. \quad (0.0.43)$$

If the volume is kept constant, the frequencies are also kept constant. Therefore, the constant volume specific heat $C_V$ is given by

$$C_V = 3Nk_B. \quad (0.0.44)$$

This is called Dulong-Petit’s law, which is independent of temperature, a contradiction to the third law of thermodynamics: $C_V \to 0$ in the $T \to 0$ limit.

Its entropy is just as (0.0.41)

$$S = 3Nk_B \log T + \text{const.} \quad (0.0.45)$$

Thus, entropy goes to $-\infty$ as $T \to 0$. This of course contradicts the third law.

0.0.19 Necessity of quantization
We must guess that $C_V \downarrow 0$ should be a quantum effect. Quantization of energy implies that you cannot pay the energy cost ‘in installments.’ Since $T$ indicates your energy payment capability, if $T$ is smaller, then quantized systems are generally harder to excite. Recall Schottky type specific heat: it goes to zero in the $T \to 0$ limit because of the energy gap: to excite the system, you must pay this amount at once.\(^9\)

0.0.20 1D quantum oscillator
Consider a collection of $3N$ 1-dimensional harmonic oscillators which are not interacting with each other at all.

Let us first examine a single oscillator of frequency $\nu$ (angular frequency $\omega = 2\pi \nu$). Elementary quantum mechanics tells us that the energy of the system is quantized as

$$\varepsilon = \left(\frac{1}{2} + n\right) \hbar \omega, \ n = 0, 1, 2, \cdots \quad (0.0.46)$$

\(^9\)At higher temperatures, the specific heat again goes to zero in this case, because there is nothing remaining to be excited; even if you are rich, now you have nothing to buy.
Each eigenstate is nondegenerate. Thus, if we specify the quantum number \( n \), the microscopic state of a single oscillator is completely specified. The canonical partition function for a single oscillator reads

\[
Z = \sum_{n=0}^{\infty} \exp \left[ -\beta \left( \frac{1}{2} + n \right) \hbar \omega \right].
\] (0.0.47)

Using \((1 - x)^{-1} = 1 + x + x^2 + x^3 + \cdots (|x| < 1)\), we get

\[
z = e^{-\beta \hbar \omega / 2}(1 - e^{-\beta \hbar \omega})^{-1} = \left( 2 \sinh \frac{\beta \hbar \omega}{2} \right)^{-1}.
\] (0.0.48)

0.0.21 Einstein model of crystal

If we may understand a 3D crystal as a collection of identical 3\( N \) independent 1D oscillators, the canonical partition function for the system should be

\[
Z = z^{3N}.
\] (0.0.49)

From (0.0.49) we obtain

\[
A(N) = 3Nk_B T \log \left( 2 \sinh \frac{\beta \hbar \omega}{2} \right),
\] (0.0.50)

and

\[
E = \frac{3}{2} N \hbar \omega \coth \left( \frac{\beta \hbar \omega}{2} \right) = 3N \left( \frac{1}{2} \hbar \omega + \frac{\hbar \omega}{e^{\beta \hbar \omega} - 1} \right).
\] (0.0.51)

Hence, the specific heat is

\[
C_V = 3Nk_B \left( \frac{\hbar \omega}{k_B T} \right)^2 \frac{e^{\beta \hbar \omega}}{(e^{\beta \hbar \omega} - 1)^2}.
\] (0.0.52)

At sufficiently high temperatures \((\hbar \omega / k_B T \ll 1)\) quantum effects should not be important. As expected we recover the classical result (0.0.44):

\[
C_V \rightarrow 3Nk_B.
\] (0.0.53)

For sufficiently low temperatures \((\hbar \omega / k_B T \gg 1)\) (0.0.52) reduces to

\[
C_V \simeq 3Nk_B \left( \frac{\hbar \omega}{k_B T} \right)^2 e^{-\beta \hbar \omega}.
\] (0.0.54)

Thus, \( C_V \) vanishes at \( T = 0 \), and the third law behavior is exhibited, but notice that this is a Schottky type specific heat due to the energy gap of size \( \hbar \omega \).

\[10^* \]

\[
\coth \frac{x}{2} = \frac{e^{x/2} + e^{-x/2}}{e^{x/2} - e^{-x/2}} = \frac{e^{x/2} - e^{-x/2} + 2e^{-x/2}}{e^{x/2} - e^{-x/2}} = 1 + \frac{2}{e^x - 1}
\]
0.0.22 Real 3D crystal: experimental

$C_V$ just obtained goes to zero exponentially fast at variance with the empirical law:

$$C_V \sim T^3. \quad (0.0.55)$$

As we know from the Schottky type specific heat it is the rule that whenever there is a finite energy gap $\varepsilon$ between the ground and the first excited states, the specific heat behaves like $\exp(-\beta \varepsilon)$ at low temperatures. The empirical result (0.0.55) implies that there is no finite energy gap in real crystals.

0.0.23 Oscillations in 3D crystal

In a real crystal there is a distribution in vibrational frequencies (= dispersion) as can be seen from Fig. 0.0.1. However, not all the vibrations contribute significantly to the low temperature heat capacity of solids.

Elastic vibrations in a crystal can be classified into two branches, optical and acoustic (Fig. 0.0.2). Only the acoustic modes are relevant. We must study the number of acoustic modes with a given angular frequency about $\omega$.

Figure 0.0.1: Above: The lowest frequency mode; Below: The highest frequency mode (for a 1D lattice).

Figure 0.0.2: The optical modes do not displace the crystal unit cells, but the acoustic modes (here a transversal mode is depicted) displace unit cells. Thus, we have only to count the number of unit cells to count the number of degrees of freedom relevant to the low temperature heat capacity (i.e., the total number of the acoustic modes).
0.0.24 How to count the number of modes
As can be seen from Fig. 0.0.1 in a 1D direction the possible wavelengths are \( \lambda = 2L, 2L/2, \ldots, 2L/N \) or in wave numbers \( k = \pi/L, 2\pi/L, \ldots, N\pi/L \). We have already seen such a sequence before: the de Broglie wave length of a free particle confined in a box which we used to study the classical ideal gas. This implies we can compute the number of modes in the volume \( V \) just as the number of eigenvalues as follows (we will encounter this approach repeatedly later, so you need not understand it now).

Let the number of modes with angular frequency between \( \omega \) and \( \omega + d\omega \) be \( D(\omega) \). Then, we have
\[
\int_0^\omega D(\omega)d\omega = \frac{1}{h^3} \int dr \int_{p\leq p(\omega)} dp,
\]
where \( p(\omega) = \hbar k = \hbar \omega/c \) (dispersion relation), and \( c \) is the sound speed. Therefore, the number of modes between \( \omega \) and \( \omega + d\omega \) is
\[
D(\omega) = \frac{V}{h^3} 4\pi p(\omega)^2 \frac{dp(\omega)}{d\omega} = 4\pi V \frac{h^3}{h^3 c^3} \omega^2 = \frac{1}{2\pi^2} \frac{V}{c^3} \omega^2.
\]

In reality, there are one longitudinal and two transversal modes for each \( \omega \), so the actual number is this times 3. In contrast to the classical gas case there are two important differences. \( D(\omega) \propto \omega^2 \) holds only for low frequency modes where the material may be regarded as an elastic continuum body. Furthermore, the wavelength cannot be indefinitely small as seen from Fig. 0.0.1. Debye introduced the following approximation:
\[
D(\omega) = A \omega^2 \Theta(\omega_D - \omega),
\]
where \( \omega_D \) is the Debye cutoff frequency (which is a materials ‘constant’ in good approximation) and \( A \) is fixed to have the total number of modes (= the total number of lattice cells \( N \times 3 \)) correctly
\[
\int_0^{\omega_D} D(\omega)d\omega = 3N.
\]
Therefore, \( A = 9N/\omega_D^3 \).

0.0.25 Debye model specific heat
Since we know the energy of the mode with \( \omega \) (0.0.51), the total energy (the internal energy due to lattice vibration) is
\[
E = \int d\omega D(\omega) \left( \frac{1}{2} \hbar \omega + \frac{\hbar \omega}{e^{\beta \hbar \omega} - 1} \right),
\]
and from (0.0.52)
\[
C_V = k_B \int d\omega D(\omega) \left( \frac{\hbar \omega}{k_B T} \right)^2 \frac{e^{\beta \hbar \omega}}{(e^{\beta \hbar \omega} - 1)^2}.
\]
Although the integration range has an upper bound \( \omega_D \), when the temperature is small, replacing this with \( \infty \) does not change the integral appreciably. Therefore, \( C_V \) behaves just as \( T^3 \) in the low temperature limit; the dimension of the integral is \( [\omega]^3 \), and we know \( [\hbar \omega/k_B T] = 1 \), so we may conclude \( [\omega]^3 \propto T^3 \) simply with the aid of dimensional analysis.
0.1 Photons, Phonons and Internal Motions

Summary
* The photon gas statistical thermodynamics is explained.
* We will guess low temperature behaviors of $E$, $S$, $\mu$ for free fermions.
* Analogy to $\mu = 0$ grand canonical ensemble may be useful, but do no read it too literally.

Key words
photon gas, Planck’s radiation formula, ultraviolet catastrophe, Stefan-Boltzmann law, internal degrees of freedom, vibrational and rotational partition functions

What you should be able to do
* You must be able to derive Planck’s formula.
* You must clearly recognize the main features of Planck’s formula.
* You must be able to itemize internal degrees of freedom of a molecule and tell their energy scales (in K).

0.1.1 Quantization of harmonic degrees of freedom
Photons and phonons are obtained through quantization of the systems that can be described as a collection of harmonic oscillators.\(^{11}\) Possible energy levels for the $i$-th mode whose angular frequency is $\omega_i$\(^{12}\) are $(n + 1/2)\hbar \omega_i$, where $n = 0, 1, 2, \cdots$. The canonical partition function of a system with modes $\{\omega_i\}$ is given by

$$Z(\beta) = \prod_i \left( \sum_{n_i=0}^{\infty} e^{-\beta(n_i+1/2)\hbar \omega_i} \right),$$

since no modes interact with each other. Here, the product is over all the modes. The sum in the parentheses gives the canonical partition function for a single harmonic oscillator, which we have already computed. The canonical partition function may be rewritten as:

$$Z(\beta) = \left[ \prod_i \left( e^{-\beta \hbar \omega_i/2} \right) \right] \prod_i \left( \sum_{n_i=0}^{\infty} e^{-\beta n_i \hbar \omega_i} \right) = \left[ \prod_i \left( e^{-\beta \hbar \omega_i/2} \right) \right] \Xi(\beta, 0).$$

$$\Xi(\beta, 0) = \prod_i \left( \sum_{n=0}^{\infty} e^{-\beta n \hbar \omega_i} \right),$$

\(^{11}\)That is, the system whose Hamiltonian is quadratic in canonical coordinates (quantum mechanically in the corresponding operators).
\(^{12}\)A system with a quadratic Hamiltonian may be described in terms of canonical coordinates (or corresponding operators) that makes the Hamiltonian diagonal. In other words, the system may be described as a collection of independent harmonic oscillators. The motion corresponding to each such harmonic oscillator is called a mode. If more than one modes have identical angular frequencies, modes cannot be uniquely chosen, but this does not cause any problem to us because partition functions need the system energies and their degeneracies only.
which may be obtained from the definition of the grand partition function by setting \( \epsilon_i = \hbar \omega_i \), and \( \mu = 0 \). As long as we consider a single system, the total zero-point energy of the system \( \sum_i \hbar \omega_i / 2 \) is constant and may be ignored by shifting the energy origin.\(^{13}\)

Therefore, the canonical partition function of the system consisting of harmonic modes (or equivalently, consisting of photons or phonons) may be written as \( \Xi_{BE}(\beta, 0) \), regarding each mode \( \hbar \omega_i \) as a single particle state energy. That is, it is written as the bosonic grand partition function with a zero chemical potential. From this observation, you should immediately recognize that \( T \) dependence of various thermodynamic quantities can be computed easily (or dimensional analytic approaches allow us to guess many \( T \)-dependent behaviors).

### 0.1.2 Warning: grand partition function with \( \mu = 0 \) is only a gimmick

The thermodynamic potential for the system consisting of photons or phonons is the Helmholtz free energy \( A \) whose independent variables are \( T \) and \( V \), because the expected number \( \langle n_i \rangle \) of phonons (photons) of mode \( i \) is determined, if the temperature \( T \) and the volume \( V \) are given. Notice that we do not have any more ‘handle’ like \( \mu \) to modify the expectation value. Since \( dA = -SdT - PdV \), we have \( A = -PV \). That is, our observation \( \log Z(\beta) = \log \Xi(\beta, 0) \) holds as a thermodynamic relation for a system that can be described by a collection of harmonic oscillators (as long as we ignore the zero-point energy). Thus, we may conclude that systems consisting of phonons or photons can be described consistently by the grand partition function with a zero chemical potential. For example, the pressure of the photon or phonon system can be computed immediately as we see below.

However, do not understand this relation to indicate that the chemical potentials of photons and phonons are indeed zero; actually they cannot be defined. The relation is only a mathematical formal relation that can be sometimes useful.\(^{14}\)

### 0.1.3 Expectation number of photons

The \( \mu = 0 \) boson analogy tells us that the average number of phonons of a harmonic mode with angular frequency \( \omega \) is given by

\[
\langle n(\omega) \rangle = \frac{1}{e^{\beta \hbar \omega} - 1}.
\] (0.1.4)

### 0.1.4 Internal energy of photon systems

The phonon contribution to the internal energy of a system may be computed just as we did for the Debye model. We need the density of states (i.e., phonon spectrum, i.e., the

\(^{13}\)Warning: However, if the system is deformed or chemical reactions occur, the system zero-point energy can change, so we must go back to the original formula with the total zero-point energy and take into account its contribution. For electromagnetic field, the change of the total zero-point energy may be observed as force. This is the Casimir effect.

\(^{14}\)Intuitively speaking, chemical potential may be defined only for particles you can ‘pick up.’ More precisely speaking, if no (conserved) charge of some kind (say, electric charge, baryon number) is associated with the particle, its chemical potential is a dubious concept.
distribution of the frequencies of the modes) $D_{ph}(\omega)$. The internal energy of all the phonons is given by

$$E = \sum_{\text{modes}} \langle n(\omega) \rangle \hbar \omega = \int d\omega D_{ph}(\omega) \frac{\hbar \omega}{e^{\beta \hbar \omega} - 1}. \quad (0.1.5)$$

This is the internal energy without the contribution of zero-point energy.

A standard way to obtain the density of states $D_{ph}(\omega)$ is to study the wave equation governing the electromagnetic waves, but here we use our usual shortcut. The dispersion relation for photons is $\epsilon = c |p| = \hbar \omega$, so

$$\int_0^\omega D_{ph}(\omega') d\omega' = \frac{V}{h^3} \int_{|p| \leq h \omega / c} d^3 p. \quad (0.1.6)$$

Here, we do not include the factor 2 due to polarization states. Differentiating the above equality, we obtain

$$D_{ph}(\omega) = \frac{4 \pi V}{h^3} \left( \frac{\hbar \omega}{c} \right)^2 \frac{\hbar}{c} = \frac{V \omega^2}{2 \pi^2 c^3}. \quad (0.1.7)$$

Photons have two polarization directions,\(^{15}\), so the actual density of the modes is this formula $\times 2$.

\textbf{0.1.5 Planck’s distribution, or radiation formula}

The internal energy $dE_\omega$ and the number $dN_\omega$ of photons in $[\omega, \omega + d\omega)$ in a box of volume $V$ are given by

$$dE_\omega = 2D_{ph}(\omega) \frac{\hbar \omega}{e^{\beta \hbar \omega} - 1} d\omega, \quad (0.1.8)$$

$$dN_\omega = 2D_{ph}(\omega) \frac{1}{e^{\beta \hbar \omega} - 1} d\omega. \quad (0.1.9)$$

The factor 2 comes from the polarization states (i.e., $D_{ph}$ here is given by (0.1.7)).

Therefore, the energy density $u(T, \omega)$ at temperature $T$ due to the photons with the angular frequencies around $\omega$ reads

$$u(T, \omega) = \frac{\omega^2}{\pi^2 c^3} \frac{\hbar \omega}{e^{\beta \hbar \omega} - 1}. \quad (0.1.10)$$

This is Planck’s radiation formula.

\textbf{0.1.6 Key features of Planck’s radiation law}

It is important to know some qualitative features of this law (Fig. 0.1.1):

(i) Planck’s law can explain why the spectrum blue-shifts as temperature increases; this was not possible within the classical theory.

\(^{15}\)Photons are spin = 1 particles, but are running always at a speed of light, so only the transversal spin components can change. Thus, the number of the spin degrees of freedom is 2 instead of 3.
Figure 0.1.1: Classical electrodynamics gives the Rayleigh-Jeans formula (0.1.12) (green); this is the result of equipartition of energy and due to many UV modes, the density is not integrable (the total energy diverges). Wien reached (0.1.13) empirically (red). Planck arrived at his formula (black) originally by interpolation of these two results. Notice that the peak position is proportional to the temperature.

(ii) The total energy density \( u(T) = E/V \) of a radiation field at temperature \( T \) is finite. \( u(T) \) is obtained by integration:

\[
u(T) = \int_0^\infty d\omega \, u(T, \omega). \tag{0.1.11}\]

With Planck’s law (0.1.10) this is always finite (we will study this later).

(iii) In the classical limit \( \hbar \to 0 \), we get

\[
u(T, \omega) = \frac{k_B T \omega^2}{\pi^2 c^3} \quad (= 2D_{ph}(\omega)k_B T), \tag{0.1.12}\]

which is the formula obtained by classical physics (i.e., the equipartition of energy). Upon integration, the classical limit gives an infinite \( u(T) \). This divergence is obviously due to the contribution from the high frequency modes. Thus this difficulty is called the ultraviolet catastrophe, which destroyed classical physics.

(iv) In the high frequency limit \( \hbar \omega \gg k_B T \) Planck’s law (0.1.10) goes to

\[
u(T, \omega) \simeq \frac{k_B T}{\pi^2 c^3} \omega^2 e^{-\beta \omega}, \tag{0.1.13}\]

which was empirically proposed by Wien.

0.1.7 Einstein’s A and B

Let us consider a system with two energy levels with energy 0 (ground state) and \( \epsilon (>0) \) (excited state). If many such systems are maintained at temperature \( T \), we know the occupation ratio of these states must be given by a Boltzmann factor \( e^{-\beta \epsilon} \). Now, let us assume that the system is also interacting with the electromagnetic field (radiation field) of frequency \( \nu = \epsilon / h \) with radiation energy density \( \rho \) (= the number density of the photons of energy \( h\nu \); no other field interacts with the system because the energy exchange is through photons of energy \( h\nu \)).\(^\text{16}\)

Interacting with the radiation field, the system may be excited at the rate \( \rho B^\dagger n_0 \), where \( n_0 \) is the number of the systems in their ground state and \( B^\dagger \) a positive constant (imagine a collisional reaction between the atom and the photon).

\(^\text{16}\)We follow the argument by Einstein in Einstein, A., (1917). Zur Quantentheorie der Strahlung, Phys. Z. 18, 121-128 [To the quantum theory of radiation].
It is also de-excited at the rate $\rho B^\dagger n_e$, where $n_e$ is the number of the systems in their excited state and $B^\dagger$ a positive constant. It is also known that there is the so-called ‘spontaneous radiation’: even if there exists no radiation field, a photon is emitted spontaneously from the excited state with the rate $A n_e$, where $A$ is a positive constant.

If $T$ is very large and the intensity of the radiation field is very strong, then $n_e \simeq n_0$, and the spontaneous radiation may be ignored relative to the induced transitions by radiation, so we must assume $B^\dagger = B^\dagger = B$, a common constant. In equilibrium there must be a transition balance between going up and going down. From this balance we get

$$B \rho n_0 = (A + B \rho)n_e. \quad (0.1.14)$$

This implies Planck’s radiation formula:

$$\rho = \frac{A/B}{e^{\beta \hbar \nu} - 1}. \quad (0.1.15)$$

0.1.8 Statistical thermodynamics of black-body radiation

Let us finish the statistical mechanics of back-body radiation.

$$u(T) = \int_0^\infty \frac{\omega^2}{\pi^2 c^3} \frac{\hbar \omega}{e^{\beta \hbar \omega} - 1} d\omega = \beta^{-4} \int_0^\infty \frac{d(\beta \omega)^2}{\pi^2 c^3} \frac{\hbar \beta \omega}{e^{\beta \hbar \omega} - 1} d(\beta \omega). \quad (0.1.16)$$

This immediately implies (as seen above)

$$u(T) \propto T^4. \quad (0.1.17)$$

which is called the Stefan-Boltzmann law.\(^{17}\)

Since we know the $T^3$-law of the phonon low temperature specific heat (the Debye theory), this should be expected. This is understandable by counting the number of degrees of freedom (Fig. ??) explained before. Although we did not calculate the proportionality constant, if you follow the above calculation you can get it. This proportionality was obtained purely thermodynamically by Boltzmann before the advent of quantum mechanics. The proportionality constant contains $\hbar$, so it was impossible to theoretically obtain the proportionality constant before Planck (Stefan experimentally obtained it).

0.1.9 Black-body equation of state

Photons may be treated as ideal bosons with $\mu = 0$,\(^{18}\) so the equation of state is immediately obtained as

$$\frac{PV}{k_B T} = \log \Xi = - \int d\epsilon D(\epsilon) \log (1 - e^{-\beta \epsilon}). \quad (0.1.18)$$

For 3D superrelativistic particles, $D(\epsilon) \propto \epsilon^2$, so

$$\int_0^\epsilon d\epsilon D(\epsilon) = \frac{1}{3} \epsilon D(\epsilon). \quad (0.1.19)$$

\(^{17}\)The proportionality constant can be computed as $k_B^4 \pi^2 / 15 \hbar^3 c^3$.

\(^{18}\)If $\mu = 0$, then $A = -PV = -k_B T \log Z$. 
This gives us (review what we did to derive $PV = 2E/3$ for ordinary particles in ??)

$$PV = \frac{1}{3}E.$$  \tag{0.1.20}

### 0.1.10 Thermodynamic derivation of black-body equation of state

Just as $PV = 2E/3$ is a result of pure mechanics, (0.1.20) is a result of pure electrodynamics, so this was known before quantum mechanics. Boltzmann started with (0.1.20) to obtain the Stefan-Boltzmann law as follows.

Since we know generally

$$E = TS - PV = TS - \frac{1}{3}E,$$  \tag{0.1.21}

$$ST = \frac{4}{3}E \text{ or } S = \frac{4E}{3T}.$$  \tag{0.1.22}

Differentiating $S$ wrt $E$ under constant $V$, noting $(\partial S/\partial E)_V = 1/T$, we obtain

$$\frac{1}{T} = -\frac{4}{3T^2} \left(\frac{\partial T}{\partial E}\right)_V E + \frac{4}{3T}$$  \tag{0.1.23}

or

$$\frac{1}{3T} = \frac{4}{3T^2} \left(\frac{\partial T}{\partial E}\right)_V E,$$  \tag{0.1.24}

that is, under constant $V$

$$\frac{dE}{E} = 4\frac{dT}{T}.$$  \tag{0.1.25}

This implies the Stefan-Boltzmann law $E \propto T^4$. The proportionality coefficient contains $\hbar$, so Boltzmann could not get it; Stefan experimentally determined the value.

### 0.1.11 Blackbody - low temperature phonon system analogy

For a phonon system of a lattice, we have a high-frequency cutoff in the energy spectrum, but its effect is almost negligible in the low temperature limit. Except for the number of modes, you must clearly recognize a direct relation between the photons in the vacuum and phonons in the crystal. Debye’s $T^3$ law is ‘almost the same’ as the Stefan-Boltzmann law.

### 0.1.12 Internal degrees of freedom of classical ideal gas

If noninteracting particles are sufficiently dilute ($\mu \ll 0$), we know classical ideal gas approximation is OK. However, the internal degrees of freedom may not be handled classically, because energy gaps may be huge. We have already glimpsed this when we discussed the gas specific heat.

Let us itemize internal degrees of freedom of a molecule:

i) Each atom has a nucleus, and its ground state could have nonzero nuclear spin. This interacts with electronic angular momentum to produce the *ultrafine structure*. The splitting
due to this effect is very small, so for the temperature range relevant to the gas phase we may assume all the levels are energetically equal. Thus, (usually) we can simply assume that the partition function is multiplied by a constant $g = \text{degeneracy of the nuclear ground state}$.

ii) Electronic degrees of freedom has a large excitation energy (of order of ionization potential $\sim$ a few eV, so unless the ground state of the orbital electrons is degenerate), we may ignore it.

iii) If a molecule contains more than one atom, it can exhibit rotational motion. The quantum of rotational energy ($\Theta_R$ below) is usually of order 10 K.

iv) Also such a molecule can vibrate. The vibrational quantum ($\Theta_V$ below) is of order 1000 K.

0.1.13 Rotation and vibration

Notice that there is a wide temperature range, including the room temperature, where we can ignore vibrational excitations and can treat rotation classically (Fig. 0.1.2). Thus, equipartition of energy applied to translational and rotational degrees of freedom can explain the specific heat of many gases.

![Figure 0.1.2: The constant volume specific heat.](image)

The Hamiltonian for the internal degrees of freedom for a diatomic molecule reads

$$H = \frac{1}{2I} J^2 + \hbar \omega \left( \hat{n} + \frac{1}{2} \right),$$  \hspace{1cm} (0.1.26)

where $I$ is the moment of inertia, $J$ the total angular momentum and $\hat{n}$ is the phonon number operator. Therefore, the partition function for the internal degrees of freedom reads

$$z_i = z_r z_v.$$  \hspace{1cm} (0.1.27)

19In the case of homonuclear diatomic molecules, nuclear spins could interfere with rotational degrees of freedom through quantum statistics, but otherwise we can simply assume as is stated in the text.

20If the ground state is degenerate, then it could have a fine structure with an energy splitting of order a few hundred K. For ground state oxygen ($^3P_2$) the splitting energy is about 200 K, so we cannot simply assume that all the states are equally probable nor that only the ground slate is relevant.

21However, for $H_2$ it is 85.4 K. For other molecules, the rotational quantum is rather small: $N_2$: 2.9 K; HCl: 15.1 K.

22$N_2$: 3340 K; $O_2$: 2260 K; $H_2$: 6100 K.
with $\Theta_R = \hbar^2/2k_B I$ and
\[ z_v = \sum_{n=0}^{\infty} e^{-(\Theta_V/T)(n+1/2)}. \] (0.1.28)

with $\Theta_V = \hbar \omega / k_B$.

0.1.14 Low and high temperature limit of rotational contribution
If the temperature is sufficiently low, then
\[ z_r \simeq 1 + 3e^{-2\Theta_R/T}. \] (0.1.29)
The contribution of rotation to specific heat is
\[ C_{\text{rot}} \simeq 3Nk_B \left( \frac{\Theta_R}{T} \right)^2 e^{-2\Theta_R/T}. \] (0.1.30)

For $T \gg \Theta_R$, we may approximate the summation by integration (Large Js contribute, so we may approximate $J \simeq J + 1$):
\[ z_r \simeq 2 \int_0^\infty dJ J e^{-J^2(\Theta_R/T)} = \frac{T}{\Theta_R}. \] (0.1.31)

This gives the rotational specific heat, but it is more easily obtained by the equipartition of energy, because the rotational energy is with a quadratic form. Thus, $C_{\text{rot}} = k_B$ in the high temperature limit.

0.1.15 Low and high temperature limit of vibrational contribution
The vibrational partition function can be summed as
\[ z_v = 1/2 \sinh(\beta\hbar \omega / 2). \] (0.1.32)

For small $T$
\[ z_v \simeq (1 + e^{-\beta\hbar \omega}) e^{\beta\hbar \omega / 2} \] (0.1.33)
is enough. Consequently,
\[ C_{\text{vib}} \sim k_B N \left( \frac{\Theta_R}{T} \right)^2 e^{-\Theta_R/T}. \] (0.1.34)

Since $\Theta_R \ll \Theta_V$, as already noted, there is a wide range of temperature where only rotation contributes to the specific heat.