# 140B Statistical Physics <br> Part 2. Quantum Gases 

## Thermal Quantum Gases

## - Bosons and Fermions

## ■ Quantum Many-Body System

Imagine our university as a quantum many-body system, where

- Each person represents a particle,
- Each role they take (be it a student, professor, staff, or service personnel) is akin to a quantum state.
- Each role describes a person's social functionality, just as each quantum state describes a particle's physical properties, such as momentum, spin, charge, color, flavor, etc.
Each particle occupies a quantum state. (like each person takes a role)
- The occupation number $n_{\alpha}=0,1,2, \ldots$ represents the number of particles occupying the $\alpha$ th quantum state (denoted as $|\alpha\rangle)$. (like the number of people in each role)
- Each quantum state $|\alpha\rangle$ also has an associated energy $\epsilon_{\alpha}$-- the cost to keep a particle in the state. (like each role in a university comes with a salary -- the cost to keep a person in their position)


## - Single-Particle v.s. Many-Body State

It is important to distinguish quantum states at two different levels:

- Single-particle state: the state or mode of a particle (like the role of a person), denoted as $|\alpha\rangle$ (with $\alpha=1,2,3, \ldots$ being the mode index).
- Many-body state: the state of a system of particles (like the role of an institute), denoted as $|\boldsymbol{n}\rangle$ with

$$
\begin{equation*}
\boldsymbol{n}:=\left\{n_{\alpha} \in \mathbb{N} \mid \alpha=1,2,3 \ldots\right\}, \tag{1}
\end{equation*}
$$

which is an integer vector that encodes occupation numbers on all available single-particle states $|\alpha\rangle$.

The many-body state $|\boldsymbol{n}\rangle$ serves as the microstate of the quantum system in the statistical mechanics context, for which we can define:

- The total number of particles in the system (like the total number of people in our university) is

$$
\begin{equation*}
N(\boldsymbol{n})=\sum_{\alpha} n_{\alpha} . \tag{2}
\end{equation*}
$$

- The total energy of the system (like the total salary expenditure of our university) is

$$
\begin{equation*}
E(\boldsymbol{n})=\sum_{\alpha} \epsilon_{\alpha} n_{\alpha} . \tag{3}
\end{equation*}
$$

[Note: to differentiate the two energies $E$ and $\epsilon_{\alpha}$, we often call $E$ the many-body energy, and $\epsilon_{\alpha}$ the single-particle energy.]

## - Identical Particles

In the quantum world, particles can be made identical, such that they can not be distinguished from one another. (This is akin to a scenario where Personal Identifiable Information (PII), like names or IDs, is protected and kept confidential. In this case, we can only talk about how many students are there in a class without revealing who they are.)

Using the math language:

- For distinguishable particles, a two-particle system can be describe by the many-body quantum state $|\alpha\rangle \otimes|\beta\rangle$, where the 1st particle is in single-particle state $|\alpha\rangle$ and the 2nd in $|\beta\rangle$.
- For identical particles, many-body states like $|\alpha\rangle \otimes|\beta\rangle$ and $|\beta\rangle \otimes|\alpha\rangle$ are indistinguishable:

| $\|\alpha\rangle \otimes\|\beta\rangle$ | $\|\beta\rangle \otimes\|\alpha\rangle$ |
| :---: | :---: |
| the 1st particle in $\|\alpha\rangle$ the 2nd particle in $\|\beta\rangle$ | the 1st particle in $\|\beta\rangle$ the 2nd particle in $\|\alpha\rangle$ |
| $\searrow$ | $\swarrow$ |
| there is one particle in $\|\alpha\rangle$, and another particle in $\|\beta\rangle$ |  |
|  |  |

The only legitimate description is $\left|1_{\alpha} 1_{\beta}\right\rangle$, as an equal-weight linear combination of $|\alpha\rangle \otimes|\beta\rangle$ and $|\beta\rangle \otimes|\alpha\rangle$. But there are still two possible ways to combine them:

- Symmetric combination $\Rightarrow$ bosons

$$
\begin{equation*}
\left|1_{\alpha} 1_{\beta}\right\rangle_{B}=\frac{1}{\sqrt{2}}(|\alpha\rangle \otimes|\beta\rangle+|\beta\rangle \otimes|\alpha\rangle), \tag{4}
\end{equation*}
$$

- Anti-symmetric combination $\Rightarrow$ fermions

$$
\begin{equation*}
\left|1_{\alpha} 1_{\beta}\right\rangle_{F}=\frac{1}{\sqrt{2}}(|\alpha\rangle \otimes|\beta\rangle-|\beta\rangle \otimes|\alpha\rangle) . \tag{5}
\end{equation*}
$$

What if we try to bring both particles to the $|\alpha\rangle$ state?

- For bosons, $\left|2_{\alpha}\right\rangle_{B}$ is still a meaningful quantum state, with the state norm enhanced by $\sqrt{2}$ due to a constructive interference:

$$
\begin{equation*}
\frac{1}{\sqrt{2}}(|\alpha\rangle \otimes|\alpha\rangle+|\alpha\rangle \otimes|\alpha\rangle)=\sqrt{2}|\alpha\rangle \otimes|\alpha\rangle=\sqrt{2}\left|2_{\alpha}\right\rangle_{B} . \tag{6}
\end{equation*}
$$

Boson enhancement factor: the probability to transfer a boson to a state that has already been occupied by $n$ bosons will get enhanced by a factor of $n+1$.
$\Rightarrow$ Bosons like to stay in the same state (exhibiting an extroverted personality).

- For fermions, the quantum state vanishes due to destructive interference.

$$
\begin{equation*}
\frac{1}{\sqrt{2}}(|\alpha\rangle \otimes|\alpha\rangle-|\alpha\rangle \otimes|\alpha\rangle)=0 . \tag{7}
\end{equation*}
$$

Pauli exclusion principle: two (or more) fermions can not occupy the same state simultaneously.
$\Rightarrow$ Fermions hate to stay in the same state (exhibiting an introverted personality).
This leads to different sets of possible values that the occupation number $n_{\alpha}$ can take:

$$
n_{\alpha}= \begin{cases}0,1,2, \ldots & \text { for bosons }  \tag{8}\\ 0,1 . & \text { for fermions }\end{cases}
$$

which results in different thermodynamic behaviors between bosons and fermions.

## - Examples of Bosons and Fermions

- Elementary particles (the Standard Model).

- Fermions are of half-integer spins.
- Bosons are of integer spins.
- Inside an atom ( ${ }^{7} \mathrm{Li}$ isotope):

- Rules (due to the multiplication rule of fermion sign):

$$
\begin{align*}
& \text { boson + boson = boson, } \\
& \text { fermion + boson = fermion, }  \tag{9}\\
& \text { fermion + fermion = boson. }
\end{align*}
$$

- Total number of fermions in an atom

$$
\begin{equation*}
N_{F}=N_{p}+N_{n}+N_{e} \stackrel{\text { neutral }}{=} 2 N_{p}+N_{n} . \tag{10}
\end{equation*}
$$

- A neutral atom is a fermion (boson) iff the number of neutrons $N_{n}$ is odd (even).


## - Statistical Distributions

## - What is Ideal Gas?

Ideal gas is a system of non-interacting (free) particles.

- Its energy is a simple sum of energies of particles in each single-particle mode

$$
\begin{equation*}
E(\boldsymbol{n})=\sum_{\alpha} \epsilon_{\alpha} n_{\alpha} . \tag{11}
\end{equation*}
$$

In real gases or more complex systems (liquids, solids), there are interactions between particles.

- The energy function will contain higher-order interaction terms

$$
\begin{equation*}
E(\boldsymbol{n})=\sum_{\alpha} \epsilon_{\alpha} n_{\alpha}+\underbrace{\sum_{\alpha \beta} \epsilon_{\alpha \beta} n_{\alpha} n_{\beta}}_{\text {two-body interaction }}+\underbrace{\sum_{\alpha \beta \gamma} \epsilon_{\alpha \beta \gamma} n_{\alpha} n_{\beta} n_{\gamma}}_{\text {three-body interaction }}+\ldots \tag{12}
\end{equation*}
$$

- The interaction, say $\epsilon_{\alpha \beta}$, is
- Attractive, if $\epsilon_{\alpha \beta}<0$ : energy is reduced when particles attract each other. (like people in a cooperative environment will reduce operational cost)
- Repulsive, if $\epsilon_{\alpha \beta}>0$ : energy is increased when particles repel each other. (like people in a confrontational environment will increase operational cost)
- If the interaction is weak $\epsilon_{\alpha \beta}, \epsilon_{\alpha \beta \gamma}, \ldots \ll \epsilon_{\alpha}$, the system can remain in the gas phase. If the interaction gets strong enough, the system may transition into liquid or solid phases.

These ideas applies to quantum particles. An ideal quantum gas refers to a system of noninteracting (free) bosons or fermions.

## - Grand Partition Function

The grand partition function is particularly convenient to study the statistical mechanics of quantum gases.

- Each microstate $|\boldsymbol{n}\rangle$ of a quantum many-body system is labeled by

$$
\begin{equation*}
\boldsymbol{n}:=\left\{n_{\alpha} \mid \alpha=1,2, \ldots\right\} . \tag{13}
\end{equation*}
$$

- Following Eq. (3) and Eq. (2), the energy and particle number functions are

$$
\begin{equation*}
E(\boldsymbol{n})=\sum_{\alpha} \epsilon_{\alpha} n_{\alpha}, N(\boldsymbol{n})=\sum_{\alpha} n_{\alpha} . \tag{14}
\end{equation*}
$$

- The probability $p(\boldsymbol{n})$ to observe the system in the microstate $|\boldsymbol{n}\rangle$ is

$$
\begin{equation*}
p(\boldsymbol{n})=\frac{1}{\mathcal{Z}} e^{-\beta(E(\boldsymbol{n})-\mu N(\boldsymbol{n}))}, \tag{15}
\end{equation*}
$$

where grand partition function $\mathcal{Z}$ is given by

$$
\begin{equation*}
Z=\sum_{n} e^{-\beta(E(n)-\mu N(n))} . \tag{16}
\end{equation*}
$$

Given that there is no interaction among single-particle states for ideal gas, the probability distribution $p(\boldsymbol{n})$ can be factorized (meaning that the distribution of each $n_{\alpha}$ is independent)

$$
\begin{equation*}
p(\boldsymbol{n})=\prod_{\alpha} p\left(n_{\alpha}\right) \tag{17}
\end{equation*}
$$

where

- The probability to observe $n_{\alpha}$ particles in the single-particle state $|\alpha\rangle$ is

$$
\begin{equation*}
p\left(n_{\alpha}\right)=\frac{1}{\mathcal{Z}_{\alpha}} \boldsymbol{e}^{-\beta\left(\epsilon_{\alpha}-\mu\right) n_{\alpha}} . \tag{18}
\end{equation*}
$$

- With the single-mode grand partition function

$$
\begin{equation*}
\mathcal{Z}_{\alpha}=\sum_{n_{\alpha}} e^{-\beta\left(\epsilon_{\alpha}-\mu\right) n_{\alpha}} . \tag{19}
\end{equation*}
$$

The full grand partition function is also factorized

$$
\begin{equation*}
\mathfrak{Z}=\prod_{\alpha} \mathcal{Z}_{\alpha} \tag{20}
\end{equation*}
$$

## Exc <br> 1

Derive Eq. (17-20) from Eq. $(15,16)$.

Or written in the logarithm form

$$
\begin{equation*}
\log \boldsymbol{Z}=\sum_{\alpha} \log \boldsymbol{Z}_{\alpha} \tag{21}
\end{equation*}
$$

- Bosons

For bosons, $n_{\alpha}=0,1,2, \ldots$ can take all natural numbers.

$$
\begin{equation*}
\boldsymbol{Z}_{\alpha}=\sum_{n_{\alpha}=0}^{\infty} e^{-\beta\left(\epsilon_{\alpha}-\mu\right) n_{\alpha}}=\frac{1}{1-e^{-\beta\left(\epsilon_{\alpha}-\mu\right)}} \tag{22}
\end{equation*}
$$

Exc
2
Evaluate the summation in Eq. (22).
Or written in the logarithm form

$$
\begin{equation*}
\log \mathcal{Z}_{\alpha}=-\log \left(1-e^{-\beta\left(\epsilon_{\alpha}-\mu\right)}\right) \tag{23}
\end{equation*}
$$

Note: the partition function is only well-defined for $\beta\left(\epsilon_{\alpha}-\mu\right)>0$ (i.e. $\left.\mu<\epsilon_{\alpha}\right)$.

## - Fermions

For fermions, $n_{\alpha}=0,1$ has only two possibilities due to the Pauli exclusion principle.

$$
\begin{equation*}
\boldsymbol{Z}_{\alpha}=\sum_{n_{\alpha}=0,1} e^{-\beta\left(\epsilon_{\alpha}-\mu\right) n_{\alpha}}=1+\boldsymbol{e}^{-\beta\left(\epsilon_{\alpha}-\mu\right)} \tag{24}
\end{equation*}
$$

Or written in the logarithm form

$$
\begin{equation*}
\log Z_{\alpha}=\log \left(1+e^{-\beta\left(\epsilon_{\alpha}-\mu\right)}\right) \tag{25}
\end{equation*}
$$

## - Bose-Einstein Distribution

Substitute the boson partition function $\mathcal{Z}_{\alpha}$ in Eq. (22) into the probability distribution $p\left(n_{\alpha}\right)$ in Eq. (18),

$$
\begin{equation*}
p\left(n_{\alpha}\right)=\left(1-e^{-\beta\left(\epsilon_{\alpha}-\mu\right)}\right) \boldsymbol{e}^{-\beta\left(\epsilon_{\alpha}-\mu\right) n_{\alpha}} \tag{26}
\end{equation*}
$$

- The distribution is tuned by a joint parameter $\beta\left(\epsilon_{\alpha}-\mu\right)$.


Based on the probability distribution Eq. (26), the average boson number $\left\langle n_{\alpha}\right\rangle$ occupying the single-particle state $|\alpha\rangle$ is

$$
\begin{equation*}
\left\langle n_{\alpha}\right\rangle=\sum_{n_{\alpha}=0}^{\infty} n_{\alpha} p\left(n_{\alpha}\right)=\frac{1}{e^{\beta\left(\epsilon_{\alpha}-\mu\right)}-1} \tag{27}
\end{equation*}
$$

Exc
3
Evaluate the summation in Eq. (27).
This is also known as the Bose-Einstein distribution.


- The Bose-Einstein distribution is well-defined only for $\epsilon_{\alpha}-\mu>0$.


## - Fermi-Dirac Distribution

Substitute the fermion partition function $\mathcal{Z}_{\alpha}$ in Eq. (24) into the probability distribution $p\left(n_{\alpha}\right)$ in Eq. (18),

$$
p\left(n_{\alpha}\right)=\frac{e^{-\beta\left(\epsilon_{\alpha}-\mu\right) n_{\alpha}}}{1+e^{-\beta\left(\epsilon_{\alpha}-\mu\right)}}= \begin{cases}\frac{1}{e^{-\beta\left(\epsilon_{-}-\mu\right)+1}} & n_{\alpha}=0  \tag{28}\\ \frac{1}{e^{\beta \beta\left(\epsilon_{e}-\mu\right)+1}} & n_{\alpha}=1\end{cases}
$$

- The distribution is tuned by a joint parameter $\beta\left(\epsilon_{\alpha}-\mu\right)$.


Based on the probability distribution Eq. (28), the average fermion number $\left\langle n_{\alpha}\right\rangle$ occupying the single-particle state $|\alpha\rangle$ is

$$
\begin{equation*}
\left\langle n_{\alpha}\right\rangle=\sum_{n_{\alpha}=0,1} n_{\alpha} p\left(n_{\alpha}\right)=\frac{1}{e^{\beta\left(\epsilon_{\alpha}-\mu\right)}+1} . \tag{29}
\end{equation*}
$$

This is also known as the Fermi-Dirac distribution.


- The Fermi-Dirac distribution is applicable for any $\epsilon_{\alpha}-\mu \in \mathbb{R}$.

Imagine a hypothetical type of identical particles (neither boson nor fermion), with the defining property that its occupation number $n_{\alpha}=0,1, \ldots, n_{\max }$ can only take values up to some integer $n_{\text {max }}$.
(i) Calculate the grand partition function $\mathcal{Z}_{\alpha}=\sum_{n_{\alpha}=0}^{n_{\max }} e^{-\beta\left(\epsilon_{\alpha}-\mu\right)} n_{\alpha}$ for such hypothetical particles on a single-particle state $|\alpha\rangle$ of energy $\epsilon_{\alpha}$.
(ii) Construct the probability distribution $p\left(n_{\alpha}\right)$ of the occupation number $n_{\alpha}$, and prove that the expectation value $\left\langle n_{\alpha}\right\rangle$ can be computed from the following derivative: $\left\langle n_{\alpha}\right\rangle:=\sum_{n_{\alpha}=0}^{n_{\max }} n_{\alpha} p\left(n_{\alpha}\right)=\beta^{-1} \partial_{\mu} \log \mathcal{Z}_{\alpha}$.
(iii) Use the derivative trick to compute $\left\langle n_{\alpha}\right\rangle$ based on the result of $\boldsymbol{Z}_{\alpha}$ obtained in problem (i). particles behave like bosons as $n_{\max } \rightarrow \infty$, and fermions as $n_{\max }=1$.


## - Maxwell-Boltzmann Distribution

Interestingly, the average occupation number $\left\langle n_{\alpha}\right\rangle$ assumes a unified form

$$
\begin{equation*}
\left\langle n_{\alpha}\right\rangle=\frac{1}{e^{\beta\left(\epsilon_{\alpha}-\mu\right)}-\eta} . \tag{30}
\end{equation*}
$$

where $\eta$ denotes the fermion sign:

$$
\eta= \begin{cases}+1 & \text { for bosons }  \tag{31}\\ -1 & \text { for fermions }\end{cases}
$$

The inverse temperature $\beta=1 / T$ is always a positive real number, and the chemical potential $\mu$ should obey:

- For bosons, the chemical potential $\mu$ can not exceed the lowest energy level (i.e. $\forall \alpha: \mu<\epsilon_{\alpha}$ ).
- For fermions, there is not restriction on the chemical potential.

Is there a "classical limit" where bosons and fermions behave the same? -- Yes, this is the limit when the gas is dilute (i.e. $N / V \rightarrow 0$ ).

- In the dilute limit, the average occupancy of each single-particle state is close to zero (compare to 1 ), i.e. $\left\langle n_{\alpha}\right\rangle \rightarrow 0$ (such that $N=\sum_{\alpha}\left\langle n_{\alpha}\right\rangle$ is also small).
- Based on Eq. (30), this limit is achieved when $\boldsymbol{e}^{\beta\left(\epsilon_{a}-\mu\right)} \rightarrow \infty$, such that the fermion sign $\eta$ in the denominator is negligible, and the average occupation number

$$
\begin{equation*}
\left\langle n_{\alpha}\right\rangle \simeq e^{-\beta\left(\epsilon_{\alpha}-\mu\right)} \tag{32}
\end{equation*}
$$

will be close to zero.
This, Eq. (32), is known as the Maxwell-Boltzmann distribution.


There will be no distinction between Bose and Fermi gases in their dilute limit (also called the classical limit, as the quantum effect that distinguish bosons and fermions is no longer important).

## - Energy and Particle Number

The average occupation number $\left\langle n_{\alpha}\right\rangle$ enables us to compute

- The average total energy (defined as $E:=\sum_{n} E(\boldsymbol{n}) p(\boldsymbol{n})$ ):

$$
\begin{equation*}
E=\sum_{\alpha} \epsilon_{\alpha}\left\langle n_{\alpha}\right\rangle=\sum_{\alpha} \frac{\epsilon_{\alpha}}{e^{\beta\left(\epsilon_{\alpha}-\mu\right)}-\eta} \tag{33}
\end{equation*}
$$

- The average total particle number (defined as $N:=\sum_{n} N(\boldsymbol{n}) p(\boldsymbol{n})$ ):

$$
\begin{equation*}
N=\sum_{\alpha}\left\langle n_{\alpha}\right\rangle=\sum_{\alpha} \frac{1}{e^{\beta\left(\epsilon_{\alpha}-\mu\right)}-\eta} \tag{34}
\end{equation*}
$$

The sign $\eta$ depends on whether the particles are bosons $(\eta=+1)$ or fermions $(\eta=-1)$.

## - Continuum Limit

## - Particles in Free Space

So far, we have not explained what labels the single-particle state $|\alpha\rangle$ and what determines its energy $\epsilon_{\alpha}$.

Consider non-interacting particles in the free space (assuming translation symmetry),
energy eigenstates are labeled by momentum $\boldsymbol{k}$ (as a good quantum number) and spin $\sigma$

$$
\begin{equation*}
\alpha=(\boldsymbol{k}, \sigma), \tag{35}
\end{equation*}
$$

- Momentum $\boldsymbol{k}=\left(k_{1}, k_{2}, \ldots, k_{D}\right)$ is a $D$-dimensional vector for particles in $D$-dimensional space.


In quantum mechanics, particles are waves, and the momentum $k_{i}$ is set by the wave length $\lambda_{i}$ via the De Broglie relation in the corresponding direction,

$$
\begin{equation*}
k_{i}=\frac{2 \pi}{\lambda_{i}}=\frac{2 \pi m_{i}}{L} \quad\left(m_{i} \in \mathbb{Z}\right), \tag{36}
\end{equation*}
$$

which must be quantized in a box of finite size $L$.

- The volume of the system (the box) will be

$$
\begin{equation*}
V=L^{D} . \tag{37}
\end{equation*}
$$

- Spin $\sigma$ labels the internal degrees of freedom of the particle. The number of spin states is called the spin degeneracy, denoted as $g_{s}$.
- Electron (spin-1/2 fermion):

$$
\begin{equation*}
g_{s}=2 . \tag{38}
\end{equation*}
$$

Two spin states: $\sigma= \pm 1 / 2$.

- Photon (spin-1 gauge boson):

$$
\begin{equation*}
g_{s}=D-1 . \tag{39}
\end{equation*}
$$

( $D-1$ ) spin (polarization) states: $\sigma= \pm 1$ for $D=3$. The $\sigma=0$ photon (longitudinal) photon is forbidden by the gauge invariance.

- Phonon (spin-1 scalar boson):

$$
\begin{equation*}
g_{s}=D \tag{40}
\end{equation*}
$$

$D$ spin (polarization) states: $\sigma=0, \pm 1$ for $D=3$.
Usually (without internal symmetry breaking), the energy $\epsilon_{\alpha}=\epsilon_{k, \sigma}$ does not depend on the spin degrees of freedom $\sigma$, so different spin states are degenerated in energy.

## - Dispersion Relations

Dispersion relation tells us how the energy $\epsilon_{k}$ of a particle (or a wave) is related to its
momentum $\boldsymbol{k}$.

- Non-relativistic particles (electrons in metal):

$$
\begin{equation*}
\epsilon_{k}=\frac{k^{2}}{2 m} \tag{41}
\end{equation*}
$$

with $m$ - the inertial mass of the particle.

- Relativistic particles (photons, acoustic phonons, electrons in graphene):

$$
\begin{equation*}
\epsilon_{k}=c|k| . \tag{42}
\end{equation*}
$$

with $c$ - the limiting speed of the particle, e.g. the speed light/sound or fermi-velocity.
(In these expressions, we have set $\hbar=1$ ).

## - Density of States

Density of state (DOS) $g(\epsilon)$ counts the number of single-particle states per volume and per energy interval $d \epsilon$ near the energy $\epsilon$ in the continuum limit, defined as the integration measure (weighting function) required to convert the state summation to an energy integration for any function $f(\epsilon)$ :

$$
\begin{equation*}
\forall f: \sum_{\alpha} f\left(\epsilon_{\alpha}\right)=V \int d \epsilon g(\epsilon) f(\epsilon) . \tag{43}
\end{equation*}
$$

For example, we can use it to compute the energy $E$ and particle number $N$ in integral forms (following Eq. (33) and Eq. (34))

$$
\begin{align*}
& E=V \int d \epsilon \frac{\epsilon g(\epsilon)}{e^{\beta(\epsilon-\mu)}-\eta} .  \tag{44}\\
& N=V \int d \epsilon \frac{g(\epsilon)}{e^{\beta(\epsilon-\mu)}-\eta} . \tag{45}
\end{align*}
$$

Similar approach applies to many other thermodynamic properties whenever a state sum is to be evaluated.

## - General Principle

Counting number of states in the momentum space:


- In this picture, each point corresponds to a state $|\boldsymbol{k}, \sigma\rangle$ in the momentum space with $g_{s}$-fold spin degeneracy. The momentum is discretized according to Eq. (36).
- The continuum limit refers to the limit $L \rightarrow \infty$, such that the states are densely distributed, forming a continuum.
- Consider a ball in the momentum space of radius $k$, its volume is

$$
\begin{align*}
& \Omega=\int_{|k|<k} d^{D} \boldsymbol{k} \\
& =\int_{0}^{k} A_{D} k^{D-1} d k  \tag{46}\\
& =\frac{A_{D}}{D} k^{D},
\end{align*}
$$

where $A_{D}$ is the area of a ( $D-1$ )-dimensional hypersphere of unit radius (in the $D$-dimensional space), given by

$$
\begin{equation*}
A_{D}=\frac{2 \pi^{D / 2}}{\Gamma(D / 2)}, \tag{47}
\end{equation*}
$$

where $\Gamma(n)=\int_{0}^{\infty} x^{n-1} e^{-x} d x$ is the Euler Gamma function.

$$
\begin{array}{c|ccccccccccc}
D & 1 & 2 & 3 & 4 & 5 & 6 & 7 & 8 & 9 & 10 & \ldots \\
\hline A_{D} & 2 & 2 \pi & 4 \pi & 2 \pi^{2} & \frac{8 \pi^{2}}{3} & \pi^{3} & \frac{16 \pi^{3}}{15} & \frac{\pi^{4}}{3} & \frac{32 \pi^{4}}{105} & \frac{\pi^{5}}{12} & \ldots
\end{array}
$$

- The number of states $\mathbf{N}_{k}$ in the ball of radius $k$ is (approximately)

$$
\begin{equation*}
\mathbf{N}_{k}=\sum_{\alpha} 1=g_{s} \sum_{|k|<k} 1=g_{s} \frac{\Omega}{\left(\frac{2 \pi}{L}\right)^{D}}=\frac{g_{s} A_{D} V}{(2 \pi)^{D} D} k^{D} . \tag{48}
\end{equation*}
$$

- On the other hand, we expect the DOS function $g(\epsilon)$ to be such that

$$
\begin{equation*}
\mathrm{N}_{k}=\sum_{\alpha} 1=V \int_{0}^{\epsilon_{k}} d \epsilon g(\epsilon) \tag{49}
\end{equation*}
$$

Therefore, comparing Eq. (48) and Eq. (49), $g(\epsilon)$ should be given by

$$
\begin{align*}
& g(\epsilon)=\frac{1}{V}\left(\frac{\partial \mathrm{~N}_{k}}{\partial \epsilon_{k}}\right)_{\epsilon_{k}=\epsilon}=\frac{1}{V}\left(\frac{\partial \mathrm{~N}_{k}}{\partial k} \frac{\partial k}{\partial \epsilon_{k}}\right)_{\epsilon_{k}=\epsilon} \\
& =\frac{g_{s} A_{D}}{(2 \pi)^{D}}\left(k^{D-1} \frac{\partial k}{\partial \epsilon_{k}}\right)_{\epsilon_{k}=\epsilon}, \tag{50}
\end{align*}
$$

which is fully determined by the dispersion relation $\epsilon_{k}$.

## - Specific Examples

- For non-relativistic particles (with the inertial mass $m$ )

$$
\begin{equation*}
g(\epsilon)=\frac{g_{s} A_{D}}{2(2 \pi)^{D}}(2 m)^{D / 2} \epsilon^{D / 2-1} . \tag{51}
\end{equation*}
$$

Exc
4
Derive Eq. (51) given the dispersion relation Eq. (41).


- For relativistic particles (with the limiting speed $c$ )

$$
\begin{equation*}
g(\epsilon)=\frac{g_{s} A_{D}}{(2 \pi)^{D}} c^{-D} \epsilon^{D-1} . \tag{52}
\end{equation*}
$$

Exc
5
Derive Eq. (51) given the dispersion relation Eq. (42).


In these examples, for particles in free space, the DOS always scales with the particle energy $\epsilon$ in a power-law manner. We might as well introduce a characteristic energy $\epsilon_{0}$ to express the DOS uniformly as

$$
\begin{equation*}
g(\epsilon)=\frac{\Delta \epsilon^{\Delta-1}}{\epsilon_{0}^{\Delta}} . \tag{53}
\end{equation*}
$$

where the exponent

$$
\begin{equation*}
\Delta=D / \zeta>0 \tag{54}
\end{equation*}
$$

depends on:

- the dimension of space $D$,
- the dynamical exponent $\zeta$ (such that $\epsilon_{k} \sim k^{\zeta}$ ):
- $\zeta=1$ for relativistic particles with linear dispersion,
- $\zeta=2$ for non-relativistic particles with quadratic dispersion.

| System | $D \zeta \Delta$ |
| :---: | :---: |
| Electrons in metal | $323 / 2$ |
| Electrons in graphene | 212 |
| Electrons in field-effect transistors | 221 |
| Electrons in nanotube | $121 / 2$ |
| Electrons on quantum Hall insulator boundary | 11 |
| Phonons in solid | 313 |
| Atomic gas | $323 / 2$ |
| Cold atoms in 2D optical tr | 22 |

Eq. (53) is designed in such a way that the integration measure takes a simple form

$$
\begin{equation*}
g(\epsilon) d \epsilon=d\left(\frac{\epsilon}{\epsilon_{0}}\right)^{\Delta}, \tag{55}
\end{equation*}
$$

assuming the single-particle energy $\epsilon \geq 0$ is non-negative. The energy scale $\epsilon_{0}$ depends on the kinetic model of the free particle,

$$
\frac{1}{\epsilon_{0}^{\Delta}}= \begin{cases}\frac{g_{s}}{\Gamma(\Delta / 2+1)}\left(\frac{1}{2 \pi^{1 / 2} c}\right)^{\Delta} & \zeta=1(\text { and } \Delta=D),  \tag{56}\\ \frac{g_{s}}{\Gamma(\Delta+1)}\left(\frac{m}{2 \pi}\right)^{\Delta} & \zeta=2(\text { and } \Delta=D / 2) .\end{cases}
$$

## Exc <br> 6 <br> Derive Eq. (56).

## - Thermodynamic Properties

## - Free Energy

The free energy plays a central role in statistical mechanics, bridging the microscopic and macroscopic realms. It is defined by the logarithmic partition function

$$
\begin{equation*}
\mathcal{F}=-T \log \mathcal{Z} . \tag{57}
\end{equation*}
$$

- According to Eq. (21), for ideal gases, the free energy arises from the independent contributions of each single-particle mode.

$$
\begin{align*}
\mathcal{F} & =-T \sum_{\alpha} \log \mathfrak{Z}_{\alpha} \\
& =\eta T V \int_{0}^{\infty} d \epsilon g(\epsilon) \log \left(1-\eta e^{-\beta(\epsilon-\mu)}\right) . \tag{58}
\end{align*}
$$

It will be convenient to introduce the fugacity

$$
\begin{equation*}
z=e^{\beta \mu}=e^{\mu / T} . \tag{59}
\end{equation*}
$$

- For bosons: $z \in(0,1)($ as $\mu<0)$.
- For fermions: $z \in(0,+\infty)$.

Using the general form of the DOS $g(\epsilon)$ in Eq. (53), the free energy can be written as

$$
\begin{equation*}
\mathcal{F}=-T V\left(\frac{T}{\epsilon_{0}}\right)^{\Delta} \mathcal{I}_{\eta}^{\Delta+1}(z) \tag{60}
\end{equation*}
$$

where $\mathcal{I}_{\eta}^{s}(z)$ is a dimensionless function of the fugacity $z=\mathscr{e}^{\mu / T}$, as defined by the following integral

$$
\begin{equation*}
\mathcal{I}_{\eta}^{s}(z):=\int_{0}^{\infty} d x \frac{x^{s-1}}{z^{-1} e^{x}-\eta} . \tag{61}
\end{equation*}
$$

- $\eta= \pm 1$ is the fermion sign ( +1 for bosons, -1 for fermions).
- $s$ counts the total power of $x$ (including $d x$ ) in the numerator.


## Exc

7
Derive and verify Eq. $(60,61)$.

- Mathematical Properties of $\mathcal{I}_{\eta}^{s}(z)$
- Expression: $I_{\eta}^{s}(z)$ can be expressed in terms of the Euler Gamma function $\Gamma(s)$ and the polylogarithm function $\operatorname{Li}_{s}(z)$

$$
\begin{equation*}
\mathcal{I}_{\eta}^{s}(z)=\frac{1}{\eta} \Gamma(s) \operatorname{Li}_{s}(\eta z), \tag{62}
\end{equation*}
$$

where $\Gamma(s)$ and $\operatorname{Li}_{s}(z)$ are defined by

$$
\begin{align*}
& \Gamma(s)=\int_{0}^{\infty} x^{s-1} e^{-x} d x \\
& \operatorname{Li}_{s}(z)=\sum_{k=1}^{\infty} \frac{z^{k}}{k^{s}} \tag{63}
\end{align*}
$$

| Exc | Verify Eq. (62) given the definition Eq. (63). |
| :---: | :--- |
| $\mathbf{8}$ |  |

- $\Gamma(s)=(s-1)$ ! can be expressed as a factorial. Therefore, it has an important property: $s \Gamma(s)=\Gamma(s+1)$.
- Graph: Behavior of $\boldsymbol{I}_{\eta}^{s}(z)$ for $\eta= \pm 1$.

- For bosons $(\eta=+1): z \in(0,1)$ and the integral function $\mathcal{I}_{+}^{s}(z)$ monotonically increases and stops (or diverges) at $z=1$.
- For fermions $(\eta=-1): z \in(0,+\infty)$ and the integral function $\mathcal{I}_{-}^{s}(z)$ monotonically increases towards $+\infty$ as $z \rightarrow+\infty$.
- When $z \rightarrow 0, \mathcal{I}_{\eta}^{s}(z)$ for both bosons and fermions converges to the same linear behavior $\mathcal{I}_{\eta}^{s}(z) \propto z$.
- Derivative: $\mathcal{I}_{\eta}^{s}(z)$ behaves like $(\log z)^{s} / s$ under differentiation

$$
\begin{equation*}
z \frac{\partial \mathcal{I}_{\eta}^{s}(z)}{\partial z} \equiv \frac{\partial \mathcal{I}_{\eta}^{s}(z)}{\partial \log z}=(s-1) \mathcal{I}_{\eta}^{s-1}(z) . \tag{65}
\end{equation*}
$$

Exc
9
Verify Eq. (65).

## - Free Energy Derivatives

As shown in Eq. (60), the (grand) free energy $\mathcal{F}$ is a function of $V, T, \mu$ (or $z=e^{\mu / T}$ ), as illustrated by the following graph


It obeys the following thermodynamic identity

$$
\begin{equation*}
d \mathcal{F}=-P d V-S d T-N d \mu, \tag{66}
\end{equation*}
$$

which enables us to compute the following thermodynamic quantities.

- Pressure

$$
\begin{equation*}
P=-\left(\frac{\partial \mathcal{F}}{\partial V}\right)_{T, \mu}=T\left(\frac{T}{\epsilon_{0}}\right)^{\Delta} I_{\eta}^{\Delta+1}(z) . \tag{67}
\end{equation*}
$$

- Entropy

$$
\begin{equation*}
S=-\left(\frac{\partial \mathcal{F}}{\partial T}\right)_{V, \mu}=V\left(\frac{T}{\epsilon_{0}}\right)^{\Delta}\left((\Delta+1) I_{\eta}^{\Delta+1}(z)-\frac{\Delta \mu}{T} I_{\eta}^{\Delta}(z)\right) . \tag{68}
\end{equation*}
$$

Exc
10
Derive Eq. (68).

- Particle number

$$
\begin{equation*}
N=-\left(\frac{\partial \mathcal{F}}{\partial \mu}\right)_{V, T}=\Delta V\left(\frac{T}{\epsilon_{0}}\right)^{\Delta} I_{\eta}^{\Delta}(z) . \tag{69}
\end{equation*}
$$

Exc
11
Derive Eq. (69).
The variable dependence among these thermodynamic quantities is summarized by the following graph:


Based on these, the energy $E$ can be reconstructed

$$
\begin{align*}
& E=\mathcal{F}+T S+\mu N \\
& =\Delta T V\left(\frac{T}{\epsilon_{0}}\right)^{\Delta} \mathcal{I}_{\eta}^{\Delta+1}(z) . \tag{70}
\end{align*}
$$

## Exc <br> 12 <br> Derive Eq. (70).

Comparing Eq. (67) and Eq. (70), we conclude that

$$
\begin{equation*}
E=\Delta P V \tag{71}
\end{equation*}
$$

which holds under all conditions regardless of bosons or fermions. For example, in $D=3$ dimensional space,

- For gas of non-relativistic particles, $E=\frac{3}{2} P V$.
- For gas of relativistic particles, $E=3 P V$.

Let us try a different way to compute the energy $E$ and the particle number $N$ for the ideal quantum gas.
(i) Starting from Eq. (33) and Eq. (34), convert the state summation to energy integration, and prove that $E$ and $N$ can be expressed as
HW
2
$E=V \int_{0}^{\infty} d \epsilon g(\epsilon) \frac{\epsilon}{e^{\beta(\epsilon-\mu)-\eta}}$,
$N=V \int_{0}^{\infty} d \epsilon g(\epsilon) \frac{1}{e^{e^{\beta(\tau-\mu)}-\eta}}$.
(ii) Plugging in the density of state $g(\epsilon)$ in Eq. (53), manipulate the integrations to the standard from in Eq. (61), and show that the results match Eq. (70) and Eq. (69)

## - Equation of State

The equation of state is an equation that relates the thermodynamic properties together, like pressure $P$, volume $V$, particle number $N$, and temperature $T$.

- A well-known example is the (classical) ideal gas law:

$$
\begin{equation*}
P V=N T, \tag{72}
\end{equation*}
$$

where the Boltzmann constant has been set to $k_{B}=1$. However, it only describe the ideal gas in the classical limit (low density and high temperature).

- Comparing Eq. (67) and Eq. (69), we found the equation of state for ideal quantum gas (free bosons and fermions)

$$
\begin{equation*}
P V=k_{\mathrm{eff}} N T, \tag{73}
\end{equation*}
$$

where the $P V / N T$ ratio is a function of fugacity $z=e^{\mu / T}$ only, denoted as

$$
\begin{equation*}
k_{\mathrm{eff}}:=\frac{P V}{N T}=\frac{I_{\eta}^{\Delta+1}(z)}{\Delta I_{\eta}^{\Delta}(z)} . \tag{74}
\end{equation*}
$$

It can be viewed as an effective Boltzmann constant (we will see that $k_{\text {eff }}=1$ for ideal classical gas as $z \rightarrow 0$ ).

## - Dilute (Classical) Limit

In the dilute limit (the classical limit), we expand $I_{\eta}^{\Delta}(z)$ around $z \rightarrow 0$ (or $\mu / T \rightarrow-\infty$ ).


$$
\begin{equation*}
\mathcal{I}_{\eta}^{s}(z) \stackrel{z \rightarrow 0}{=} \Gamma(s)\left(z+\frac{\eta}{2^{s}} z^{2}+\ldots\right) . \tag{75}
\end{equation*}
$$

Exc
13

> Verify Eq. (75).

Using Eq. (75), around $z \rightarrow 0, k_{\text {eff }}$ and $N$ behaves as

$$
\begin{align*}
& k_{\mathrm{eff}}=1-\frac{\eta z}{2^{\Delta+1}}+\ldots, \\
& N=V\left(\frac{T}{\epsilon_{0}}\right)^{\Delta} \Gamma(\Delta+1) z+\ldots \tag{76}
\end{align*}
$$

Exc
14
Verify the expansions in Eq. (76).
We can solve $z$ in terms of $N / V$ and substitute the solution to $k_{\text {eff }}$, this gives the virial expansion of the equation of state

$$
\begin{equation*}
\frac{P V}{N T}=\left(1-\frac{\eta}{2^{\Delta+1} \Gamma(\Delta+1)} \frac{N}{V}\left(\frac{\epsilon_{0}}{T}\right)^{\Delta}+\ldots\right) \tag{77}
\end{equation*}
$$

- The deviation from the ideal classical gas behavior $(P V=N T)$ will be significant when $(N / V)\left(\epsilon_{0} / T\right)^{\Delta} \gg 1$, i.e. when
- the temperature is low $(T \rightarrow 0)$,
- or the density is high $(N / V \rightarrow \infty)$.
- Bose statistics $(\eta=+1)$ causes an decrease in pressure compare to the classical limit, as if there is an effective attraction between bosons.

- Fermi statistics $(\eta=-1)$ causes an increase in pressure compare to the classical limit, as if there is an effective repulsion between fermions.



## - Isothermal Process

Isothermal (constant-temperature) process is the thermodynamic process where $T$ and $N$ are fixed, i.e. the system in quasi-equilibrium with a thermal bath $(d T=0)$ and there is no particle exchange ( $d N=0$ ).

Given a fixed particle number $N$, Eq. (67) and Eq. (69) tell us how to compute pressure $P$ and volume $V$ as a function of temperature $T$ and fugacity $z$

$$
\begin{align*}
& P(T, z)=T\left(\frac{T}{\epsilon_{0}}\right)^{\Delta} I_{\eta}^{\Delta+1}(z) \\
& V(T, z)=N\left(\Delta\left(\frac{T}{\epsilon_{0}}\right)^{\Delta} I_{\eta}^{\Delta}(z)\right)^{-1} . \tag{78}
\end{align*}
$$

Fix $T$, and vary $z$, the point $(V(T, z), P(T, z))$ traces out a curve in the $P-V$ plane, called the isothermal curve. The system will move along the isothermal curve in the isothermal process.

- For bosons $(\eta=+1)$, the isothermal curves are like

- For fermions $(\eta=-1)$, the isothermal curves are like


In the classical limit, isothermal curves follow $P V=N T=$ const. However, as $N / V \rightarrow \infty$ or $T \rightarrow 0$, isothermal curves deviates from the classical behavior in distinct ways,

- Degenerated Bose gas: the curves flatten out at low volumes, suggesting transitions to Bose-Einstein condensates (BEC), where pressure cease to increase as more and more bosons condense to a zero-momentum state that does not contribute to pressure.
- Degenerated Fermi gas: even at zero temperature, fermions can sustain a finite pressure, called the degeneracy pressure, due to the Pauli exclusion principle preventing fermions from occupying the same quantum state.


## - Specific Heat

Specific heat is the amount of heat (per particle) required to change the temperature of a system. There are two types of specific heat for systems of fixed particle number:

- Isochoric (constant-volume) specific heat

$$
\begin{equation*}
c_{V}=\frac{T}{N}\left(\frac{\partial S}{\partial T}\right)_{N, V} . \tag{79}
\end{equation*}
$$

It can be computed by evaluating $S$ as a function of $T$ given $N, V$ fixed.


- Given $N, V$, input $T$.
- Solve for $z$ from $N(V, T, z)=N$.
- Output $S=S(V, T, z)$.
- Isobaric (constant-pressure) specific heat

$$
\begin{equation*}
c_{P}=\frac{T}{N}\left(\frac{\partial S}{\partial T}\right)_{N, P} \tag{80}
\end{equation*}
$$

It can be computed by evaluating $S$ as a function of $T$ given $N, P$ fixed.


- Given $N, P$, input $T$.
- Solve for $z$ from $P(T, z)=P$.
- Solve for $V$ from $N(V, T, z)=N$.
- Output $S=S(V, T, z)$.

For Bose gas, their behaviors are like:



For Fermi gas, their behaviors are like:



## - Dilute (Classical) Limit

In the dilute limit (the classical limit), we expand $I_{\eta}^{\Delta}(z)$ around $z \rightarrow 0$ (or $\left.\mu / T \rightarrow-\infty\right)$,


Using the expansion formula Eq. (75), we find

$$
\begin{align*}
P & =T\left(\frac{T}{\epsilon_{0}}\right)^{\Delta} \Gamma(\Delta+1) z+\ldots  \tag{81}\\
S & =V\left(\frac{T}{\epsilon_{0}}\right)^{\Delta} \Gamma(\Delta+1)(1+\Delta-\log z) z+\ldots \tag{82}
\end{align*}
$$

$$
\begin{equation*}
N=V\left(\frac{T}{\epsilon_{0}}\right)^{\Delta} \Gamma(\Delta+1) z+\ldots \tag{83}
\end{equation*}
$$

## Exc <br> 15 <br> Verify the expansions in Eq. $(81,82,83)$.

- To compute the isochoric (constant volume) specific heat, $N$ and $V$ are held fixed. First solve $z$ from Eq. (83),

$$
\begin{equation*}
z=\frac{1}{\Gamma(\Delta+1)} \frac{N}{V}\left(\frac{\epsilon_{0}}{T}\right)^{\Delta}, \tag{84}
\end{equation*}
$$

then substitute Eq. (84) to Eq. (82), to the leading order,

$$
\begin{equation*}
S=N(\Delta \log T+\log V-\log N)+\text { const. } \tag{85}
\end{equation*}
$$

## Exc <br> 16 <br> Derive Eq. (85).

therefore, $c_{V}=(\partial S / \partial \log T)_{N, V} / N$ is

$$
\begin{equation*}
c_{V}=\Delta . \tag{86}
\end{equation*}
$$

- To compute the isobaric (constant pressure) specific heat, $N$ and $P$ must be fixed. First solve $z$ from Eq. (81),

$$
\begin{equation*}
z=\frac{1}{\Gamma(\Delta+1)} \frac{P}{T}\left(\frac{\epsilon_{0}}{T}\right)^{\Delta}, \tag{87}
\end{equation*}
$$

then substitute Eq. (87) to Eq. (82), to the leading order,

$$
\begin{equation*}
S=N((\Delta+1) \log T-\log P)+\text { const. } \tag{88}
\end{equation*}
$$

## Exc <br> 17 <br> Derive Eq. (88).

therefore, $c_{P}=(\partial S / \partial \log T)_{N, P} / N$ is

$$
\begin{equation*}
c_{P}=\Delta+1 . \tag{89}
\end{equation*}
$$

Following the same approach, one may also compute $c_{V}$ and $c_{P}$ to the next order in $z$,

$$
\begin{align*}
& c_{V}=\Delta+\frac{\eta}{2^{\Delta+1} \Gamma(\Delta-1)} \frac{N}{V}\left(\frac{\epsilon_{0}}{T}\right)^{\Delta}+\ldots, \\
& c_{P}=\Delta+1+\frac{\eta(\Delta+1)}{2^{\Delta+1} \Gamma(\Delta)} \frac{P}{T}\left(\frac{\epsilon_{0}}{T}\right)^{\Delta}+\ldots \tag{90}
\end{align*}
$$

## Exc <br> 18 <br> Derive Eq. (90).

The relations like $c_{P}-c_{V}=1$ and $c_{P} / c_{V}=1+1 / \Delta$ are only valid in the dilute (classical) limit, which do not apply to quantum gases in general.

## - Adiabatic Process

Adiabatic process is the thermodynamic process where $S$ and $N$ are fixed, i.e. no heat transfer $(d S=0)$ and no particle exchange ( $d N=0$ ).

The adiabatic process of ideal gas is described by

$$
\begin{equation*}
P V^{\gamma}=\text { const. } \tag{91}
\end{equation*}
$$

where $\gamma$ is the adiabatic exponent:

$$
\begin{equation*}
\gamma=1+1 / \Delta . \tag{92}
\end{equation*}
$$

## Exc

19
Prove the statement Eq. (91, 92).
It holds beyond the classical limit and applies to generic ideal quantum gases. For example, when $\Delta=3 / 2$, we have $\gamma=5 / 3$-- a familiar result for ideal gases.

## - Summary

|  |  | Bose gas | Fermi gas Classical limit |  |
| :---: | :---: | :---: | :---: | :---: |
| Energy | $E=\Delta P V$ | $\checkmark$ | $\checkmark$ | $\checkmark$ |
| Eq. of state | $P V=k_{\text {eff }} N T$ | $k_{\text {eff }}<1$ | $k_{\text {eff }}>1$ | $k_{\text {eff }}=1$ |
| Specific heat | $c_{V}$ | $\left(\sim T^{\Delta}\right)_{T \rightarrow 0}$ | $(\sim T)_{T \rightarrow 0}$ | $\Delta$ |
|  | $c_{P}$ | $0_{T \rightarrow 0}$ | $(\sim T)_{T \rightarrow 0}$ | $\Delta+1$ |
| Isochoric | $V=$ const. | $\checkmark$ | $\checkmark$ | $\checkmark$ |
| Isobaric | $P=$ const. | $\checkmark$ | $\checkmark$ | $\checkmark$ |
| Isothermal | $P V=$ const. | $\times$ | $\times$ | $\checkmark$ |
| Adiabatic | $P V^{\gamma}=$ const. | $\checkmark$ | $\checkmark$ | $\checkmark$ |
|  | $(\gamma=1+1 / \Delta)$ |  |  |  |

- In reality, gases are consist of quantum particles (either bosons or fermions) at the microscopic level. $\Rightarrow$ The classical gas is not real.
- However, in the dilute limit, both Bose and Fermi gases converge to a universal behavior described by the classical gas. Given $z \propto(N / V)\left(\epsilon_{0} / T\right)^{\Delta}$ [see Eq. (84)], the classical limit $(z \rightarrow 0)$ is characterized by

$$
\begin{equation*}
\frac{N}{V}\left(\frac{\epsilon_{0}}{T}\right)^{\Delta} \ll 1 \tag{93}
\end{equation*}
$$

In the following, we will move away from the classical limit, and explore the intriguing realm of degenerated quantum gases.

## Degenerated Quantum Gases

## - Degenerated Bose Gas

## - Unsustainable Thermal Bosons

Let us now understand the elephant in the room: what happens to the Bose gas at low temperature?

Consider $N$ bosons in a volume $V$, recalling Eq. (45), the number density $N / V$ should be given by the following integral

$$
\begin{equation*}
\frac{N}{V}=\int_{0}^{\infty} d \epsilon \frac{g(\epsilon)}{e^{\beta(\epsilon-\mu)}-1} . \tag{94}
\end{equation*}
$$

- $g(\epsilon)=\Delta \epsilon^{\Delta-1} / \epsilon_{0}^{\Delta}$ is the (per volume) density of states.
- As the temperature $T=1 / \beta$ lowers, the chemical potential $\mu$ (or the fugacity $z=e^{\mu / T}$ ) will adjust to maintain the number density $N / V($ say $N / V=1)$.


However, the constraint $\mu<0$ (or $z<1$ ) sets a limit for the adjustment.

- It is possible that the integral can not provide the required $N / V$, even if the chemical potential is tuned to $\mu=0$. To see this, we investigate the divergent behavior of the integrand near $\epsilon \rightarrow 0$,

$$
\begin{equation*}
\frac{N}{V} \propto \int_{0}^{\infty} d \epsilon \frac{\epsilon^{\Delta-1}}{e^{\epsilon / T}-1} \stackrel{\epsilon \rightarrow 0}{\sim} T \int_{0}^{\cdots} \frac{d \epsilon}{\epsilon^{2-\Delta}} . \tag{95}
\end{equation*}
$$

- If $\Delta>1$, the integral will converge (even if $\mu=0$ ), which can not provide the required $N / V$ as $T$ lowers to a certain point.
- If $\Delta \leq 1$, the integral can diverge (if $\mu=0$ ), which enables the adjustment of $\mu$ to reach the required $N / V$ no matter how low $T$ is.
It seems that bosons will disappear at low temperature. Where do the "missing" bosons go?
- The integral Eq. (94) only accounts for the thermal bosons (bosons occupying the excited states).
- Due to the vanishing DOS as $\epsilon \rightarrow 0$, the bosons occupying the lowest-energy ground state $(\epsilon=0)$ was not taken into account.
To be more careful, the number of bosons should contain two parts

$$
\begin{equation*}
N=N_{\mathrm{th}}+N_{0} \tag{96}
\end{equation*}
$$

- $N_{\text {th }}$ : the thermal boson number, defined by the integral Eq. (94), whose result is given by Eq. (69),

$$
\begin{equation*}
N_{\mathrm{th}}=\Delta V\left(\frac{T}{\epsilon_{0}}\right)^{\Delta} I_{+}^{\Delta}(z) . \tag{97}
\end{equation*}
$$

- $N_{0}$ : the condensed boson number (in the ground state), given by the Bose-Einstein distribution $n_{B}(\epsilon)=\left(z^{-1} e^{\beta \epsilon}-1\right)^{-1}$ at $\epsilon=0$ :

$$
\begin{equation*}
N_{0}=\frac{1}{z^{-1}-1} \tag{98}
\end{equation*}
$$

meaning that the fugacity will be set by $z=N_{0} /\left(N_{0}+1\right)$.
Now there is no problem keeping $N$ fixes: when $N_{\text {th }}$ becomes insufficient to host all $N$ bosons by thermal excitations, the $N_{0}=N-N_{\text {th }}$ remaining bosons will condense to the ground state.

## - Bose-Einstein Condensation

Bose-Einstein condensation (BEC) is the phenomenon that a macroscopic number of bosons occupies the lowest-energy single-particle state at low temperature. The corresponding state of matter is called Bose-Einstein condensate.

- By saying that the ground state occupation number $N_{0}$ is macroscopic, we mean

$$
\begin{equation*}
\lim _{V \rightarrow \infty} \frac{N_{0}}{V} \neq 0 \tag{99}
\end{equation*}
$$

This is unusual, as for other excited states, the occupation number does not scale with the system size $V$ (i.e. $\left\langle n_{\alpha}\right\rangle / V \rightarrow 0$ as $V \rightarrow \infty$ ).

- The fraction of thermal v.s. condensed (ground-state) bosons:


The condensate fraction in the BEC phase

$$
\begin{equation*}
\frac{N_{0}}{N}=1-\left(\frac{T}{T_{c}}\right)^{\Delta} . \tag{100}
\end{equation*}
$$

## Exc

- The BEC transition temperature $T_{c}$ is set by the temperature at which $z \rightarrow 1$,

$$
\begin{equation*}
T_{c}=\epsilon_{0}\left(\frac{1}{\Gamma(\Delta+1) \zeta(\Delta)} \frac{N}{V}\right)^{1 / \Delta}, \tag{101}
\end{equation*}
$$

where $\zeta(s):=\operatorname{Li}_{s}(1)$ is the Riemann zeta function, defined by

$$
\zeta(s)=\sum_{k=1}^{\infty} \frac{1}{k^{s}} .
$$

Exc

- For non-relativistic particles,

$$
\begin{equation*}
T_{c}=\frac{2 \pi}{m}\left(\frac{1}{\zeta(D / 2)} \frac{N}{V}\right)^{2 / D} . \tag{102}
\end{equation*}
$$

To increase the BEC transition temperature, one can

- either reduce the boson mass $m$,
- or increase the boson density $N / V$.
- Dimension dependence of $T_{c}$ (following Eq. (102))


BEC transition only happens in 3D and higher dimensions (for non-relativistic bosons).

- In general, BEC transition only happens in bosonic systems with $\Delta=D / \zeta>1$. According to Eq. (101), $T_{c} \rightarrow 0$ as $\Delta \rightarrow 1_{+}$due to the divergence of the Riemann zeta function $\zeta(\Delta \rightarrow 1) \rightarrow \infty$.

In the BEC phase (when $T<T_{c}$ ), the pressure $P$ of the Bose gas will gradually decrease to zero as the temperature $T$ is lowered. Show that they follow a power law $P=A T^{\lambda}$, where
(ii) and determine the power $\lambda$ in terms of the exponent $\Delta=D / \zeta$ that appears in the density of state.

## - Ultracold Atoms

The Bose-Einstein condensate (BEC) of weakly interacting atoms was observed in ultracold atom systems, where atoms are trapped by lasers and cooled to extremely low temperatures.

- Examples are found in bosonic atoms, such as $\mathrm{Rb}, \mathrm{Na}$, Li, of a number $N \sim 10^{4} \rightarrow 10^{7}$ below the temperature $T_{c} \sim 10^{-7} \mathrm{~K}$. [2001 Nobel Prize]
How do we know whether the temperature was really that low?
Traditional thermometers become ineffective in measuring such extremely low temperature, leading researchers to infer temperature by observing the Bose-Einstein distribution directly!

A time-of-flight (TOF) experiment was performed, involving the following steps:

- Release of Atoms: Initially, the atoms are confined in an optical trap. The trap (trapping laser) is tuned off, allowing atoms to expand freely.
- Free Expansion: The atoms expand for a set duration. During this time, their positions evolve according to their initial momenta: atoms with larger momenta will travel further.
- Imaging: Following the expansion period, the spatial distribution of the atoms is captured using imaging techniques. This image reflects the momentum distribution of the atoms.

[1] K. B. Davis, M. -O. Mewes, M. R. Andrews, N. J. van Druten, D. S. Durfee, D. M. Kurn, and W. Ketterle, Bose-Einstein Condensation in a Gas of Sodium Atoms, Phys. Rev. Lett. 75, 3969 (1995)

The expected number of atoms carrying momentum $\boldsymbol{k}$ is given by the Bose-Einstein distribution:

$$
\begin{equation*}
N_{k}=\frac{1}{e^{\beta\left(\epsilon_{k}-\mu\right)}-1}, \tag{103}
\end{equation*}
$$

where $\epsilon_{\boldsymbol{k}}=\boldsymbol{k}^{2} /(2 m)$ is kinetic energy of the atom.

- Aggregating within each momentum shell $4 \pi k^{2} d k$ gives the distribution for the momentum magnitude $k \equiv|\boldsymbol{k}|$ :

$$
\begin{equation*}
N_{k}=\frac{4 \pi k^{2}}{\exp \left(\frac{1}{T}\left(\frac{k^{2}}{2 m}-\mu\right)\right)-1} . \tag{104}
\end{equation*}
$$

- However, this only accounts for the thermal boson. One should also include the potential contribution from $N_{0}$ bosons condensed in the ground state.

$$
\begin{equation*}
N_{k}=\frac{4 \pi k^{2}}{\exp \left(\frac{1}{T}\left(\frac{k^{2}}{2 m}-\mu\right)\right)-1}+N_{0} \delta(k) . \tag{105}
\end{equation*}
$$



The peak at $k=0$ (artificially broadened for visualization) represents the condensed bosons in the lowest-energy state.

## - Condensation Transition

The BEC transition refers to the phase transition between the BEC phase (where $N_{0} / V \neq 0$ ) and the normal phase (where $N_{0} / V=0$ ) in the thermodynamic limit $V \rightarrow \infty$.

- Near the BEC transition, the fugacity is close to one. So we expand $I_{+}^{\Delta}(z)$ around $z \rightarrow 1$.


$$
\mathcal{I}_{+}^{s}(z) \stackrel{z \rightarrow 1}{=} \begin{cases}-\log (1-z) & \text { if } s=1  \tag{106}\\ \frac{\pi^{2}}{6}+(1-z)(\log (1-z)-1)+\ldots & \text { if } s=2 \\ \Gamma(s)(\zeta(s)-\zeta(s-1)(1-z)+\ldots)+\frac{\pi}{\sin \pi s}(1-z)^{s-1}+\ldots & \text { otherwise. }\end{cases}
$$

[^0]Verify Eq. (106).
Let us focus on the case of non-relativistic bosons in $D=3$ dimension, corresponding to $\Delta=D / 2=3 / 2$.

- The expansion Eq. (106) enables us to compute the thermal boson number $N_{\text {th }}$ [see Eq. (69)] and the energy $E$ [see Eq. (70)]:

$$
N_{\mathrm{th}}=\frac{3 \sqrt{\pi} \zeta(3 / 2)}{4} V\left(\frac{T}{\epsilon_{0}}\right)^{3 / 2}\left(1-\frac{2 \sqrt{\pi}}{\zeta(3 / 2)} \sqrt{1-z}+\ldots\right),
$$

$$
E=\frac{9 \sqrt{\pi} \zeta(5 / 2)}{8} T V\left(\frac{T}{\epsilon_{0}}\right)^{3 / 2}\left(1-\frac{\zeta(3 / 2)}{\zeta(5 / 2)}(1-z)+\ldots\right) .
$$

## Exc <br> 23

Derive Eq. (107).

- These expressions in Eq. (107) are not very friendly. Let us simplify them by introducing:
- The BEC transition temperature $T_{c}$ (adapt from Eq. (101) or Eq. (102)),

$$
\begin{equation*}
T_{c}=\epsilon_{0}\left(\frac{4}{3 \sqrt{\pi} \zeta(3 / 2)} \frac{N}{V}\right)^{2 / 3} . \tag{108}
\end{equation*}
$$

- The energy $E_{c}$ of the system at $T=T_{c}$,

$$
\begin{equation*}
E_{c}=\frac{9 \sqrt{\pi} \zeta(5 / 2)}{8} T_{c} V\left(\frac{T_{c}}{\epsilon_{0}}\right)^{3 / 2}=\frac{3}{2 B} N T_{c} . \tag{109}
\end{equation*}
$$

- Two numerical constants $A$ and $B$,

$$
\begin{align*}
& A=\frac{2 \sqrt{\pi}}{\zeta(3 / 2)} \approx 1.35697,  \tag{110}\\
& B=\frac{\zeta(3 / 2)}{\zeta(5 / 2)} \approx 1.94737 .
\end{align*}
$$

Then Eq. (107) can be organized into a relatively neat form:

$$
\begin{align*}
& \frac{N_{\mathrm{th}}}{N}=\left(\frac{T}{T_{c}}\right)^{3 / 2}(1-A \sqrt{1-z}),  \tag{111}\\
& E=E_{c}\left(\frac{T}{T_{c}}\right)^{5 / 2}(1-B(1-z)) . \tag{112}
\end{align*}
$$

- The behavior of the fugacity $z$ near the transition can be analyzed as follows:
- When $T>T_{c}, N_{\text {th }}=N$ (thermal excitations can host all bosons), then $z$ can be determined by solving Eq. (111),

$$
\begin{equation*}
1=\left(\frac{T}{T_{c}}\right)^{3 / 2}(1-A \sqrt{1-z}) \tag{113}
\end{equation*}
$$

whose solution is

$$
\begin{equation*}
z=1-\frac{1}{A^{2}}\left(1-\left(\frac{T_{c}}{T}\right)^{3 / 2}\right)^{2} . \tag{114}
\end{equation*}
$$

- When $T<T_{c}$, it is no longer possible for $N_{\text {th }}$ to match $N$. The remaining $N_{0}=N-N_{\text {th }}$ bosons will condense. In this case, $z=N_{0} /\left(N_{0}+1\right) \rightarrow 1$ will become very close to 1 (given that $N_{0}$ is macroscopically large).

This behavior can be summarized as

$$
\begin{equation*}
z=1-\frac{1}{A^{2}} \max \left(0,1-\left(\frac{T_{c}}{T}\right)^{3 / 2}\right)^{2} \tag{115}
\end{equation*}
$$



Note that the piecewise nature of $z$ (as a function of $T$ ) is the fundamental reason that leads to singularities in various thermodynamic functions at $T=T_{c}$, as will be seen later.

- Plugging the solution Eq. (115) to Eq. (112), we obtain the energy $E$ as a function of temperature $T$ (with fixed $N$ and $V$, packed in $T_{c}$ and $E_{c}$ )

$$
\begin{equation*}
E=E_{c}\left(\frac{T}{T_{c}}\right)^{5 / 2}\left(1-\frac{B}{A^{2}} \max \left(0,1-\left(\frac{T_{c}}{T}\right)^{3 / 2}\right)^{2}\right) \tag{116}
\end{equation*}
$$



The key indicator of a phase transition is hidden in the higher order derivatives of the energy with respect to the phase transition driving parameter (which, in this case, is the temperature $T$ ).

- 1st order derivative: (isochoric) heat capacity -- the amount of heat (per particle) required to change the temperature.

$$
\begin{equation*}
C_{V}=\left(\frac{\partial E}{\partial T}\right)_{N, V} . \tag{117}
\end{equation*}
$$

Show that the heat capacity $C_{V}$ in Eq. (117) is related to the specific heat $c_{V}$ in Eq.
24
(79) by $C_{V}=c_{V} N$.


The heat capacity exhibits a cusp at $T=T_{c}$, which is rooted in the similar cusp behavior in $(\partial z / \partial T) \sim \max \left(0,1-\left(T_{c} / T\right)^{3 / 2}\right)$.

- 2nd order derivative: starts to exhibit a discontinuity at $T=T_{c}$.



## Classification of Phase Transitions:

An $\boldsymbol{n}$ th order phase transition is a phase transition at which the energy (or free energy) starts to exhibit singularity (discontinuity or divergence) at its $n$th order derivative with respect to the driving parameter.

- 1st order phase transitions:
- Boiling of water
- Melting of ice
- Structural transitions in some materials
- 2nd order (or continuous) phase transitions:
- BEC transitions
- Superconducting transitions
- Magnetic transitions in some materials
- Liquid crystal transitions
- 3rd order phase transitions:
(They are less common or more theoretical.)
- Certain topological quantum phase transitions (e.g. mass generation transition of 2D Dirac fermions)
- Infinite order phase transitions:
- Berezinskii-Kosterlitz-Thouless (BKT) transitions (e.g. superfluid transition in 2D) [2016 Nobel Prize]


## - Superfluid Helium

${ }^{4} \mathrm{He}$ (the most abundant isotope of helium) is a bosonic atom. It has two liquid phases:


- A classical liquid (normal fluid) phase, called He-I: finite viscosity, limited heat conductivity, staying in its container normally.
- A quantum liquid (superfluid) phase, called He-II: zero viscosity, nearly infinite thermal conductivity, can spontaneously climb walls and escape its container.

The phase transition between $\mathrm{He}-\mathrm{I}$ and He -II phases is called the $\lambda$-transition, due to the $\lambda$ shape (logarithmic divergence) of the specific heat at the critical point.


There is a close connection between BEC and superfluidity:

- BEC refers to the condensate of non-interacting bosons (gas),
- Superfluid is the condensate of (repulsively) interacting bosons (liquid).

They shares some common features, such as macroscopic boson occupation in the lowest-energy state. However, the interaction is essential to maintain the quantum coherence among condensed bosons, such that they can propagate collectively in the form of a macroscopic matter wave -- the key feature of superfluidity.

## - Black-Body Radiation

## - Radiations Carried by Bosons

Radiation is the emission or transmission of energy in the form of waves (= particles) through the space.

- Electromagnetic radiation (light) is carried by photons (spin-1).
- Acoustic radiation (sound) is carried by phonons (spin-0).
- Spin wave radiation is carried by magnons (spin-1).
- Gravitational radiation is carried by gravitons (spin-2).
- *Dark matter radiation could hypothetically be carried by axions (spin-0).

All these particles are bosons (given their integer spins).
Black-body radiation is an ideal Bose gas of radiation-carrying bosons in thermal equilibrium with a heat bath (i.e. the "black body" that can absorb and emit radiation).

- The physical laws of black-body radiation applies to all different types of radiations, although we will mainly focus on photons gas in the following discussions.

Examples:

| System | $T$ | Dominant radiation |
| :---: | :---: | :---: |
| Cosmic microwave background (CMB) | 2.7 K | Microwave |
| Cold interstellar dusts | $\sim 10 \mathrm{~K}$ | Terahertz |
| Night hemisphere of the Earth | 300 K | Infrared |
| Electric stove/oven | 500 K | Infrared |
| Incandescent light | 2500 K | Infrared to Visible |
| The Sun | 6000 K | Visible |
| Black hole accretion disk | $\sim 10^{6} \mathrm{~K}$ | X-ray |

## - Zero Chemical Potential for Radiations

A key feature of radiations is that there is no particle number conservation for the radiationcarrying bosons.

- This is because a heat bath could absorb one high-energy boson and emit two lower-energy bosons (causing boson number to +1 ), or vice versa (causing boson number to -1 ).
- For examples, atoms can serve as heat bath to absorb and emit photons.

- In such processes,
- while energy remains conserved $\Rightarrow\langle E\rangle=E$,
- the particle number does not $\Rightarrow\langle N\rangle=$ ??.
- If the particle number is not a conserved quantity, we should not require a definitive expectation value for the number of particles in the system. Therefore, the grand canonical ensemble is not a good starting point for our discussion.
However, having already embarked on a journey with the grand canonical ensemble, do we need to start all over again?
-- No panic. In statistical mechanics, whenever faced with questions we can't answer, we take the answer that maximizes entropy.
- Our problem: how to infer the chemical potential $\mu$ with no knowledge about the particle number $N$.
- According to Eq. (68), the entropy $S$ is related to chemical potential $\mu$ (or the fugacity $\left.z=e^{\mu / T}\right)$ by

$$
\begin{equation*}
S=V\left(\frac{T}{\epsilon_{0}}\right)^{\Delta}\left((\Delta+1) I_{+}^{\Delta}(z)-\Delta I_{+}^{\Delta-1}(z) \log z\right) . \tag{118}
\end{equation*}
$$

Given $V$ and $T$ fixed, $S$ is a monotonically increasing function of $z \in(0,1)$ for any choice of $\Delta>0$.


Exc
25
Prove that $S$ is a monotonically increasing function of $z \in(0,1)$.
The entropy $S$ is always maximized at $z=1$, corresponding to

$$
\begin{equation*}
\mu=0 . \tag{119}
\end{equation*}
$$

- The chemical potential is always zero for radiation-carrying bosons.
- In fact, there is no need to introduce the chemical potential $\mu$ as a Lagrangian multiplier in the first place, if the statistical ensemble is not constrained by the particle number $N$.


## - Spectral Energy Density

The spectral energy density $\rho(\omega)$ describes how the radiation energy density $E / V$ is distributed over different frequencies $\omega$, as defined by

$$
\begin{equation*}
\frac{E}{V}=\int \rho(\omega) d \omega . \tag{120}
\end{equation*}
$$

- In quantum mechanics, due to the wave-particle duality, the radiation frequency $\omega$ is related to the boson single-particle energy $\epsilon$ by

$$
\begin{equation*}
\epsilon=\hbar \omega . \tag{121}
\end{equation*}
$$

(We may set $\hbar=1$ ).

- Knowing that radiations are carried by bosons $(\eta=+1)$ of zero chemical potential ( $\mu=0$ ), Eq. (44) implies that the spectral energy density for the black-body radiation should take the following form

$$
\begin{gather*}
\rho(\omega)=\frac{\omega g(\omega)}{\mathfrak{e}^{\beta \omega}-1} \\
=\frac{\Delta}{\epsilon_{0}^{\Delta}} \frac{\omega^{\Delta}}{e^{\beta \omega}-1} . \tag{122}
\end{gather*}
$$

Further assuming relativistic gauge bosons in $D=3$ dimensional space (such as photons), we obtain the Planck radiation law:

$$
\begin{equation*}
\rho(\omega)=\frac{1}{\pi^{2} c^{3}} \frac{\omega^{3}}{\boldsymbol{e}^{\beta \omega}-1} . \tag{123}
\end{equation*}
$$

Exc
26
Derive Eq. (122) and Eq. (123).


The spectral distribution $\rho(\omega)$ has a maximum at the frequency

$$
\begin{equation*}
\omega_{m} \approx 2.821 T \tag{124}
\end{equation*}
$$

Exc
27

```
Derive Eq. (124).
```

Thus the dominant frequency of thermal radiation will shift towards higher frequency linearly with the raising temperature, known as the Wien's displacement law.

## - Thermodynamic Properties

Given the zero chemical potential $\mu=0$ (or unit fugacity $z=1$ ), thermodynamic quantities of the black-body radiation takes simple forms [see Eq. (67-70) and Eq. (60)].

## - Pressure

$$
\begin{equation*}
P=\kappa T^{\Delta+1} \tag{125}
\end{equation*}
$$

## - Entropy

$$
\begin{equation*}
S=(\Delta+1) \kappa V T^{\Delta} . \tag{126}
\end{equation*}
$$

- Particle number

$$
\begin{equation*}
N=\frac{\zeta(\Delta)}{\zeta(\Delta+1)} \kappa V T^{\Delta} \tag{127}
\end{equation*}
$$

## - Energy

$$
\begin{equation*}
E=\Delta \kappa V T^{\Delta+1} \tag{128}
\end{equation*}
$$

- Free energy $(F=E-T S=\mathcal{F}+\mu N)$

$$
\begin{equation*}
F=\mathcal{F}=-\kappa V T^{\Delta+1}, \tag{129}
\end{equation*}
$$

The constant $\kappa$ is defined as

$$
\begin{equation*}
\kappa=\frac{1}{\epsilon_{0}^{\Delta}} \Gamma(\Delta+1) \zeta(\Delta+1) . \tag{130}
\end{equation*}
$$

Derive Eq. (125-130).

Based on these results, we can conclude a few important thermodynamic relations for blackbody radiations.

- Equation of state:

$$
\begin{equation*}
P V=\frac{\zeta(\Delta+1)}{\zeta(\Delta)} N T, \tag{135}
\end{equation*}
$$

which deviated from ideal classical gas behavior $(P V=N T)$ by a factor $\zeta(\Delta+1) / \zeta(\Delta)$. For relativistic bosons in three dimensional space, we have $\Delta=3$, and $\zeta(4) / \zeta(3) \approx 0.9004$, a bit smaller than 1 .

- In terms of energy $E$,

$$
\begin{equation*}
E=\Delta \kappa V T^{\Delta+1} \tag{136}
\end{equation*}
$$

we can express

$$
\begin{align*}
& P V=\frac{1}{\Delta} E, \\
& T S=\left(1+\frac{1}{\Delta}\right) E,  \tag{137}\\
& F=-\frac{1}{\Delta} E .
\end{align*}
$$

- Thermodynamics processes:

| Process | Relation | Notes |
| :--- | :--- | :--- |
| Isobaric | $P=$ const. | as $P$ and $T$ are locked together by $P=\kappa T^{\Delta+1}$ |
| Isothermal | $T=$ const. |  |
| Isochoric | $V=$ const. |  |
| Adiabatic | $P V^{\gamma}=$ const. | with $\gamma=1+1 / \Delta$ |

## - Specific Heat

Since particle number is not conserved in radiation gas, it is only meaningful to define the specific heat as the heat capacity per volume.

- Isochoric (constant-volume) specific heat

$$
\begin{equation*}
c_{V}=\frac{T}{V}\left(\frac{\partial S}{\partial T}\right)_{V}=\left(1+\frac{1}{\Delta}\right) \kappa T^{\Delta} . \tag{138}
\end{equation*}
$$

It exhibits a $c_{V} \sim T^{\Delta}$ behavior, a important feature of radiation gas.

- Isobaric (constant-pressure) specific heat can not be defined as making $P$ constant prevents us to change $T$.


## - Degenerated Fermi Gas

## - Fermi Energy

In the $T \rightarrow 0$ low-temperature limit, the Fermi-Dirac distribution is simply a step function:

$$
\left\langle n_{\alpha}\right\rangle=\frac{1}{e^{\beta\left(\epsilon_{\alpha}-\mu\right)}+1} \xrightarrow{T \rightarrow 0} \begin{cases}1 & \text { for } \epsilon_{\alpha}<\mu,  \tag{139}\\ 0 & \text { for } \epsilon_{\alpha}>\mu .\end{cases}
$$



- Each fermion added to the system will just fill up the available single-particle states from low energy to high energy.
- The energy of the last filled state is called the Fermi energy, defined by the chemical potential at $T=0$,

$$
\begin{equation*}
\epsilon_{F}:=\mu(T=0) . \tag{140}
\end{equation*}
$$

The Fermi energy is set by the fermion density $N / V$ in the system. To see this, we compute the number of fermions $N$ following Eq. (45),

$$
\begin{align*}
& N=V \int d \epsilon \frac{g(\epsilon)}{e^{\beta(\epsilon-\mu)}+1} \\
& \stackrel{T \rightarrow 0}{=} V \int_{0}^{\epsilon_{F}} d \epsilon g(\epsilon) . \tag{141}
\end{align*}
$$

For free particles, recall Eq. (55): $g(\epsilon) d \epsilon=d\left(\epsilon / \epsilon_{0}\right)^{\Delta}$, the energy integral simply results in

$$
\begin{equation*}
N=V\left(\frac{\epsilon_{F}}{\epsilon_{0}}\right)^{\Delta}, \tag{142}
\end{equation*}
$$

which determines the Fermi energy,

$$
\begin{equation*}
\epsilon_{F}=\epsilon_{0}\left(\frac{N}{V}\right)^{1 / \Delta} . \tag{143}
\end{equation*}
$$

- While $\epsilon_{F}$ is the highest energy that a fermion can take, the average energy $E / N$ carried by a fermion is a fraction of $\epsilon_{F}$, given by

$$
\begin{equation*}
E=\frac{\Delta}{\Delta+1} N \epsilon_{F} \tag{144}
\end{equation*}
$$

Exc
29

> Derive Eq. (144).

It goes as $E=\frac{3}{5} N \epsilon_{F}$ for $\Delta=\frac{3}{2}$ (for non-relativistic fermions in three dimensional space).

- Given $E=\Delta P V[$ recall Eq. (71)], the pressure $P$ of the degenerated Fermi gas (at $T=0$ ) is

$$
\begin{equation*}
P=\frac{1}{\Delta+1} \frac{N}{V} \epsilon_{F} \tag{145}
\end{equation*}
$$

Amazingly, $P$ does not vanish at zero temperature for Fermi gas (unlike the ideal classical gas $P V=N T)$.

- The finite pressure of Fermi gas at low temperature is called the degeneracy pressure.
- It is a consequence of Pauli exclusion principle and is important in understanding the stability of white dwarf stars and neutron stars in astrophysics.

Although these results were derived in the $T \rightarrow 0$ limit, the picture hold as the temperature $T \ll T_{F}$ is low compared to the Fermi temperature $T_{F}$, defined as the temperature scale corresponding to the Fermi energy:

$$
\begin{equation*}
T_{F}=\frac{\epsilon_{F}}{k_{B}} . \tag{146}
\end{equation*}
$$

- Under the setting of $k_{B}=1$, temperature and energy are essentially the same unit, with

$$
\begin{equation*}
1.60218 \times 10^{-19} \mathrm{~J}=1 \mathrm{eV}=11604.5 \mathrm{~K} \simeq 10^{4} \mathrm{~K} . \tag{147}
\end{equation*}
$$

- $T_{F}$ can vary by orders of magnitudes in different systems:

| System | $\epsilon_{F}$ | $T_{F}$ | $T$ |
| :---: | :---: | :---: | :---: |
| Ultracold ${ }^{6} \mathrm{Li}$ atoms | $\sim 0.1 \mathrm{neV}$ | $\sim 10^{-6} \mathrm{~K}$ | $\sim 10^{-7} \mathrm{~K}$ |
| Superfluid ${ }^{3} \mathrm{He}$ atoms | $\sim 0.1 \mathrm{meV}$ | $\sim 1 \mathrm{~K}$ | $\sim 10^{-3} \mathrm{~K}$ |
| Electrons in metal | $\sim 1 \mathrm{eV}$ | $\sim 10^{4} \mathrm{~K}$ | 300 K |
| Electrons in white dwarf stars | $\sim 0.1 \mathrm{MeV}$ | $\sim 10^{9} \mathrm{~K}$ | $\sim 10^{6 \sim 8} \mathrm{~K}$ |
| Nucleons in atomic nucleus | $\sim 10 \mathrm{MeV} \sim 10^{11} \mathrm{~K}$ | -- |  |
| Neutrons in neutron starts | $\sim 0.1 \mathrm{GeV} \sim 10^{12} \mathrm{~K} \sim 10^{6 \sim 11} \mathrm{~K}$ |  |  |

## - Compact Stars

Compact stars, such as white dwarfs, neutron stars, and black holes, are endpoints of stellar evolution. In the Hertzsprung-Russell (HR) Diagram of astrophysics, stars are plotted according to their luminosity and temperature:


- Main sequence stars: the majority of stars, including the Sun, in stable phase of stellar evolution, fusing H into He in their cores.
- White dwarf stars: remnants of low to medium mass stars, like our Sun, no nuclear fusion anymore and are supported against gravitational collapse by electron degeneracy pressure.
- Neutron stars: remnants of supernova from more massive stars, gravity is strong enough to push electrons into nucleus,

$$
\begin{equation*}
p+e^{-} \rightarrow n+v_{e}, \tag{148}
\end{equation*}
$$

leaving neutrons alone to fight against gravitational collapse by neutron degeneracy pressure. (Too faint to be visible on the HR diagram.)

- Black holes: extremely dense remnants formed from the gravitational collapse of very massive stars post-supernova. Nothing can sustained against gravity, even light can not escape.

For a white dwarf star of mass $M$ and radius $R$, its energy consists of

$$
\begin{equation*}
E=E_{\text {gas }}+E_{\text {grav }} \tag{149}
\end{equation*}
$$

- The energy of the degenerated electron gas

$$
\begin{equation*}
E_{\mathrm{gas}}=\frac{\Delta}{\Delta+1} N \epsilon_{F} \propto \frac{M^{1+1 / \Delta}}{R^{3 / \Delta}} . \tag{150}
\end{equation*}
$$

Exc
Verify Eq. (150).

- The gravitational energy

$$
\begin{equation*}
E_{\text {grav }} \propto-\frac{M^{2}}{R} . \tag{151}
\end{equation*}
$$

Put together, the balance is achieved when the energy $E$ in Eq. (149) is minimized, which gives a relationship between the radius $R$ and the mass $M$ of the star:

$$
\begin{equation*}
R \sim M^{\frac{1-\Delta}{3-\Delta}} . \tag{152}
\end{equation*}
$$

```
Derive Eq. (152).
```

- For non-relativistic electrons: $\Delta=3 / 2$, Eq. (152) predicts

$$
\begin{equation*}
R \sim M^{-1 / 3}, \tag{153}
\end{equation*}
$$

meaning that the star will shrink as it gets more massive.

- Because as $M$ increases, gravity compresses the star more, forcing electrons to get closer, generating a higher degeneracy pressure (Fermi energy) to balance the stronger gravity, thus resulting in a smaller star radius $R$.
- However, this trend does not sustain for ever. As $\epsilon_{F}$ grows to the point that it becomes comparable to the electron rest mass energy $m_{e} c^{2}$, relativity effects sets in.
- For relativistic electrons: $\Delta=3$, Eq. (152) predicts

$$
\begin{equation*}
R \sim M^{\infty} \tag{154}
\end{equation*}
$$

a strange expression ... but it just means $M \sim R^{0}=$ const., i.e. $M$ will top out when $R$ reduces to the point that electrons become relativistic.

- In the relativistic regime, the Fermi gas energy ( $E_{\text {gas }} \sim R^{-1}$ ) does not increase as rapidly as it does in the non-relativistic regime $\left(E_{\text {gas }} \sim R^{-2}\right)$. Consequently, there comes a point where the pressure can no longer counterbalance the gravity for a more massive star.
This leads to a mass limit, called the Chandrasekhar limit, about 1.44 of the solar mass $M_{\odot}$,

$$
\begin{equation*}
M_{\text {limit }} \approx 1.44 M_{\odot} \tag{155}
\end{equation*}
$$

Beyond this limit, the white dwarf can no longer sustain itself against gravitational collapse, potentially leading to:

- a type Ia supernova (the "standard candle" in astronomy),
- or a more compact object, like a neutron star or a black hole.

Similar analysis can be made for neutron stars. While for black holes, one needs a different analysis to see $R=2 G M / c^{2}$ as predicted by General Relativity. Put together the massradius relations for different compact stars:


This helps us understand the fate of the Sun. After exhausting its nuclear fuel, it will:

- first expand into a red giant (swallowing the Earth),
- then blow away its outer layers,
- leaving behind a white dwarf (cooling over time).


## - Low-Temperature Expansion

To better understand the low-temperature $\left(T \ll T_{F}\right)$ behavior of Fermi gas, we should study the function $\mathcal{I}_{-}^{s}(z)$ in the $z \rightarrow \infty$ limit. Because when $T / \epsilon_{F} \rightarrow 0$, we have

$$
\begin{equation*}
z=e^{\mu / T} \simeq e^{\epsilon_{F} / T} \rightarrow+\infty . \tag{156}
\end{equation*}
$$

Expanding $I_{-}^{\Delta}(z)$ in the $z \rightarrow \infty$ limit is called the low-temperature expansion (or the Sommerfeld expansion).


$$
\begin{equation*}
\mathcal{I}_{-}^{s}(z) \stackrel{z \rightarrow \infty}{=} \frac{(\log z)^{s}}{s}\left(1+\frac{\pi^{2} s(s-1)}{6(\log z)^{2}}+\frac{7 \pi^{4} s(s-1)(s-2)(s-3)}{360(\log z)^{4}}+\ldots\right) \tag{157}
\end{equation*}
$$

32
Verify Eq. (157).

- The expansion Eq. (157) enables us to compute the fermion number $N$ [see Eq. (69)] and the energy $E$ [see Eq. (70)] at low temperature,

$$
\begin{align*}
& N=V\left(\frac{\mu}{\epsilon_{0}}\right)^{\Delta}\left(1+\frac{\pi^{2} \Delta(\Delta-1)}{6}\left(\frac{T}{\mu}\right)^{2}+\ldots\right)  \tag{158}\\
& E=\frac{\Delta}{\Delta+1} \mu V\left(\frac{\mu}{\epsilon_{0}}\right)^{\Delta}\left(1+\frac{\pi^{2} \Delta(\Delta+1)}{6}\left(\frac{T}{\mu}\right)^{2}+\ldots\right) \tag{159}
\end{align*}
$$

Exc
33
Derive Eq. (158), Eq. (159).

- For fixed fermion number $N$, we can solve Eq. (158) for the chemical potential $\mu$,

$$
\begin{equation*}
\mu=\epsilon_{F}\left(1-\frac{\pi^{2}(\Delta-1)}{6}\left(\frac{T}{\epsilon_{F}}\right)^{2}+\ldots\right) \tag{160}
\end{equation*}
$$

where $\epsilon_{F}=\epsilon_{0}(N / V)^{1 / \Delta}$ is the Fermi energy.

## Exc <br> 34 <br> Derive Eq. (160).

- We can see $\mu=\epsilon_{F}$ at $T=0$, as expected.
- As $T$ increases, $\mu$ will deviates from $\epsilon_{F}$ slowly, in quadratic order of $T / \epsilon_{F}$.
- Substitute the solution of $\mu$ in Eq. (160) to the expression of $E$ in Eq. (159), we obtain $E$ as a function of $T$ at fixed $N$ and $V$.

$$
\begin{equation*}
E=\frac{\Delta}{\Delta+1} N \epsilon_{F}\left(1+\frac{\pi^{2}(\Delta+1)}{6}\left(\frac{T}{\epsilon_{F}}\right)^{2}+\ldots\right) . \tag{161}
\end{equation*}
$$

## Exc

35
Derive Eq. (161).

## - Specific Heat

The energy function $E$ in Eq. (161) enables us to compute the (isochoric) specific heat.
Following the definition

$$
\begin{equation*}
c_{V}=\frac{1}{N}\left(\frac{\partial E}{\partial T}\right)_{N, V}, \tag{162}
\end{equation*}
$$

the result reads

$$
\begin{equation*}
c_{V}=\frac{\pi^{2} \Delta}{3}\left(\frac{T}{\epsilon_{F}}\right)+\ldots \tag{163}
\end{equation*}
$$

```
Derive Eq. (163).
```

- The specific heat of a Fermi gas is linear in $T$ at low temperature.
- Recall Eq. (86) that $c_{V}=\Delta$ is the result for a classical gas. Compare to that, the specific heat of a degenerated Fermi gas is smaller by a factor of $T / \epsilon_{F}$ (or $T / T_{F}$ ).
The specific heat essentially counts the number of modes (per particle) that can be thermally excited to participate in energy exchange.
- In classical gas, every particle can participate in energy exchange with the heat bath.
- In degenerated Fermi gas, only a $T / \epsilon_{F}$ fraction of the fermions near the Fermi surface are excited and can contribute to the energy exchange. The remaining fermions deep in the Fermi sea are effective frozen.

The specific heat will deviate from the low-temperature linear- $T$ behavior if $T$ approaches to $\epsilon_{F}$ (or $T_{F}$ ), and eventually saturate to the classical limit.


## - Susceptibilities

Number susceptibility is the (relative) rate that the particle number $N$ changes with the chemical potential $\mu$, defined by

$$
\begin{equation*}
\chi_{N}=\frac{1}{N}\left(\frac{\partial N}{\partial \mu}\right)_{V, T} . \tag{164}
\end{equation*}
$$

To the leading order in the $T \rightarrow 0$ limit,

$$
\begin{equation*}
\chi_{N}=\frac{\Delta}{\epsilon_{F}}+\ldots \tag{165}
\end{equation*}
$$

## Exc

```
Derive Eq. (165).
```

The number susceptibility forms a basis to compute other susceptibilities of the Fermi gas in response to different external fields.

Electron is a fermion that carries both charge ( $-e$ ) and spin $\hbar / 2$ (which corresponds to a magnetic moment $\mu_{B}=e \hbar /\left(2 m_{e}\right)$, known as a Bohr magneton). These properties enables electron gas to response to both electric and magnetic fields.

- Charge susceptibility: the rate that the charge density $Q / N$ changes with the electric potential $\mathcal{E}$.

$$
\begin{equation*}
\chi_{Q}=\frac{1}{N}\left(\frac{\partial Q}{\partial \mathcal{E}}\right)_{V, T} . \tag{166}
\end{equation*}
$$

- The total charge of the electron gas is

$$
\begin{equation*}
Q=-e N . \tag{167}
\end{equation*}
$$

- Varying in electric potential $d \mathcal{E}$ will cause a change in the electron chemical potential by
$d \mu=-e d \mathcal{E}$.
- Therefore, $\chi_{Q}$ is related to $\chi_{N}$ by

$$
\begin{equation*}
\chi_{Q}=e^{2} \chi_{N}=\frac{\Delta e^{2}}{\epsilon_{F}}+\ldots \tag{169}
\end{equation*}
$$

- Spin susceptibility: the rate that the magnetization density $M / N$ changes with the magnetic field $B$.

$$
\begin{equation*}
\chi_{M}=\frac{1}{N}\left(\frac{\partial M}{\partial B}\right)_{V, T} . \tag{170}
\end{equation*}
$$

- The total magnetization of the electron gas is
$M=\mu_{B}\left(N_{\uparrow}-N_{\downarrow}\right)$,
where $N_{\uparrow}$ and $N_{\downarrow}$ are respectively the number of up-spin and down-spin electrons in a magnetic field.
- Varying the magnetic field $d B$ will cause a change in the chemical potential for up-spin and down-spin electrons,

$$
\begin{align*}
& d \mu_{\uparrow}=\mu_{B} d B, \\
& d \mu_{\downarrow}=-\mu_{B} d B . \tag{172}
\end{align*}
$$

- Therefore, $\chi_{M}$ is related to $\chi_{N}$ by

$$
\begin{equation*}
\chi_{M}=\mu_{B}^{2} \chi_{N}=\frac{\Delta \mu_{B}^{2}}{\epsilon_{F}}+\ldots . \tag{173}
\end{equation*}
$$

This is also known as the Pauli susceptibility, which (partially) explains the paramagnetism of many metals.

The charge and spin susceptibilities can be measured in experiments by putting the electron gas in an electromagnetic field, thereby providing a feasible approach to infer the number susceptibility (which is otherwise not directly measurable).

Note: the specific heat $c_{V}$ and different susceptibilities $\chi_{Q}, \chi_{M}$ are all proportional to $\Delta / \epsilon_{F}$ in
the $T \rightarrow 0$ limit:

$$
\begin{align*}
& c_{V}=\frac{\pi^{2} \Delta}{3}\left(\frac{T}{\epsilon_{F}}\right)+\ldots, \\
& \chi_{Q}=\frac{\Delta e^{2}}{\epsilon_{F}}+\ldots  \tag{174}\\
& \chi_{M}=\frac{\Delta \mu_{B}^{2}}{\epsilon_{F}}+\ldots,
\end{align*}
$$

By taking ratios among them, the non-universal feature like $\epsilon_{F}$ can be eliminated, resulting in an universal ratio, call the Wilson ratio.

$$
\begin{equation*}
R_{W}=\frac{\pi^{2}}{3} \frac{\chi_{Q} T}{e^{2} c_{V}}=\frac{\pi^{2}}{3} \frac{\chi_{M} T}{\mu_{B}^{2} c_{V}}=1 \tag{175}
\end{equation*}
$$

- For non-interacting electrons, the Wilson ratio is expected to be unity. This prediction holds for most metals, where electron-electron interactions are well screened and thus negligible.
- However, deviations from unity in the Wilson ratio are indicative of significant electronelectron interactions within the materials. -- A defining feature of strongly correlated electron systems, including many unconventional high-temperature superconductors.

Thermoelectric (Seebeck) effect is an interesting phenomenon that temperature difference across a metal can induce a voltage difference. The Seebeck coefficient $\mathcal{S}$ characterizes how electric potential $\mathcal{E}$ raises with temperature $T$, defined as
$\mathcal{S}=\left(\frac{\partial \mathcal{E}}{\partial T}\right)_{Q, V}$.
(i) Express the Seebeck coefficient in terms of the temperature derivative of chemical potential.
(ii) Use Eq. (160) to calculate the Seebeck coefficient $\mathcal{S}$ to the leading order of $T / \epsilon_{F}$ at low-temperature.
(iii) Show that the ratio $R_{S}=e \mathcal{S} / c_{V}$ between the Seebeck coefficient $\mathcal{S}$ and the specific heat $c_{V}$ is a universal ratio (that does not depend on the Fermi energy $\epsilon_{F}$ to the leading order in $T / \epsilon_{F}$ ).

## Summary

## - Partition Function is All You Need

## - General Idea

The partition function (or the free energy) is all you need in statistical physics.

- Given the energy function $E(x)$ for some random variable $\boldsymbol{x}$.
- Under maximal entropy estimation, the equilibrium probability distribution of $\boldsymbol{x}$ is given by the exponential form, with $\beta=1 / T$,

$$
\begin{equation*}
p(\boldsymbol{x})=\frac{1}{Z} e^{-\beta E(x)} . \tag{176}
\end{equation*}
$$

- The partition function $Z$ is not just a normalization constant

$$
\begin{equation*}
Z=\sum_{x} e^{-\beta E(x)}, \tag{177}
\end{equation*}
$$

its also encodes all the thermodynamic properties of the statistical ensemble.

- Or equivalently, in terms of the free energy $F$

$$
\begin{equation*}
F=-T \log Z \tag{178}
\end{equation*}
$$

The trick is to take advantage of the nice form of $\log Z$ under derivatives.

- Derivative of $\log Z$ with respect to $\beta$, energy expectation value is obtained,

$$
\begin{equation*}
\frac{\partial \log Z}{\partial \beta}=-\langle E(\boldsymbol{x})\rangle . \tag{179}
\end{equation*}
$$

Exc
38
Derive Eq. (179).

- Suppose the energy function $E_{\lambda}(\boldsymbol{x})$ further depends on a Lagrangian multiplier $\lambda$ for a function $f(\boldsymbol{x})$ of $\boldsymbol{x}$

$$
\begin{equation*}
E(\boldsymbol{x}) \rightarrow E_{\lambda}(\boldsymbol{x})=E(\boldsymbol{x})+\lambda f(\boldsymbol{x}), \tag{180}
\end{equation*}
$$

derivative of $\log Z$ with respect to $\lambda$ gives the expectation value of $f(\boldsymbol{x})$

$$
\begin{equation*}
\frac{\partial \log Z}{\partial \lambda}=-\beta\langle f(\boldsymbol{x})\rangle . \tag{181}
\end{equation*}
$$

## Exc <br> 39 <br> Derive Eq. (181).

Or more directly as

$$
\begin{equation*}
\frac{\partial F}{\partial \lambda}=\langle f(\boldsymbol{x})\rangle \tag{182}
\end{equation*}
$$

Conclusion: to evaluate the expectation value of any function $f(\boldsymbol{x})$, first add a term $\lambda f(\boldsymbol{x})$ to the energy function $E(\boldsymbol{x})$, compute the free energy $F$, and take the derivative $\partial_{\lambda} F$ with respect to $\lambda$.

## - Cumulant Expansion

One can continue to take higher order derivatives of $F$ to obtain other derived thermodynamic properties.

- To be more systematic, the first few orders of derivatives of $\log Z$ are given by (denote $\partial / \partial \lambda$ as $\partial_{\lambda}$ )

$$
\begin{aligned}
& \quad \partial_{\lambda} \log Z=\frac{\partial_{\lambda} Z}{Z}, \\
& \\
& \partial_{\lambda}^{2} \log Z=\frac{\partial_{\lambda}^{2} Z}{Z}-\left(\frac{\partial_{\lambda} Z}{Z}\right)^{2}, \\
& \\
& \partial_{\lambda}^{3} \log Z=\frac{\partial_{\lambda}^{3} Z}{Z}-3 \frac{\partial_{\lambda}^{2} Z}{Z} \frac{\partial_{\lambda} Z}{Z}+2\left(\frac{\partial_{\lambda} Z}{Z}\right)^{2}, \\
& \\
& \cdots
\end{aligned}
$$

- The partition function derivatives are related to different moments of $f(x)$,

$$
\begin{equation*}
\frac{\partial_{\lambda}^{n} Z}{Z}=\left\langle(-\beta f(\boldsymbol{x}))^{n}\right\rangle, \tag{184}
\end{equation*}
$$

for $n=1,2,3, \ldots$.
Exc
41
Prove Eq. (184).
Substitute Eq. (184) into Eq. (183), the derivatives of $\log Z$ gives us different cumulants of $f(x)$,

$$
\begin{aligned}
& \partial_{\lambda} \log Z=-\beta\langle f(\boldsymbol{x})\rangle, \\
& \partial_{\lambda}^{2} \log Z=(-\beta)^{2}\left(\left\langle f(\boldsymbol{x})^{2}\right\rangle-\langle f(\boldsymbol{x})\rangle^{2}\right), \\
& \partial_{\lambda}^{3} \log Z=(-\beta)^{3}\left(\left\langle f(\boldsymbol{x})^{3}\right\rangle-3\left\langle f(\boldsymbol{x})^{2}\right\rangle\langle f(\boldsymbol{x})\rangle+2\langle f(\boldsymbol{x})\rangle^{3}\right), \\
& \ldots
\end{aligned}
$$

They corresponds to the mean, variance, skewness of $f(\boldsymbol{x})$.
Example: particle number fluctuation.
Grand canonical ensemble can be effectively viewed as a canonical ensemble, if we tread $E(\boldsymbol{n})-\mu N(\boldsymbol{n})$ energy function (where $\boldsymbol{n}=\left\{n_{\alpha} \mid \alpha=1,2, \ldots\right\}$ denotes the collection of occupation numbers on each single-particle state).

- The particle number fluctuation is quantified by the variance of $N(\boldsymbol{n})$,

$$
\begin{align*}
& \operatorname{var} N:=\left\langle N(\boldsymbol{n})^{2}\right\rangle-\langle N(\boldsymbol{n})\rangle^{2} \\
& =(-\beta)^{-2} \partial_{\mu}^{2} \log Z  \tag{186}\\
& =-T \frac{\partial^{2} F}{\partial \mu^{2}}
\end{align*}
$$

- The particle number susceptibility is defined as Eq. (164)

$$
\begin{equation*}
\chi_{N}=\frac{1}{N}\left(\frac{\partial N}{\partial \mu}\right)=-\frac{1}{N} \frac{\partial^{2} F}{\partial \mu^{2}}, \tag{187}
\end{equation*}
$$

given that $N=-\partial_{\mu} F$.
Therefore, there is a relation between fluctuation and susceptibility (response)

$$
\begin{equation*}
\operatorname{var} N=N T \chi_{N} \tag{188}
\end{equation*}
$$

This is an example for the fluctuation-response relation, which states that the thermal fluctuation of an extensive variable (like var $N$ ) is always proportional to the response of the extensive variable (like $N$ ) with respect the its conjugate intensive variable (like $\mu$ ).

## - Mid-Term Sample Problem

In our universe, every matter has its anti-matter counterpart. Consider a ideal gas system of particles and anti-particles, suppose each single particle state $|\alpha\rangle$ can be either empty ( $n_{\alpha}=0$ ), or occupied by one particle $\left(n_{\alpha}=1\right)$ or one anti-particle $\left(n_{\alpha}=-1\right)$, i.e. $n_{\alpha}=-1,0,1$ (and no further options).

- Both particle and anti-particle occupations cost the same amount of energy $\epsilon_{\alpha}$ on the $|\alpha\rangle$ state, while the empty occupation does not cost energy.
- Anti-particle counts as a "negative" particle in terms of particle number, as it can annihilate with the particle.

| $n_{\alpha}$ | $N$ | $E$ | meaning |
| :---: | :---: | :---: | :---: |
| 1 | 1 | $\epsilon_{\alpha}$ | particle |

$\begin{array}{llll}0 & 0 & 0 & \text { empty }\end{array}$
$-1-1 \epsilon_{\alpha}$ anti-particle
Given a collection of occupation numbers $\boldsymbol{n}=\left\{n_{\alpha}\right\}$, the energy and particle numbers will be given by

$$
\begin{align*}
& E(\boldsymbol{n})=\sum_{\alpha} \epsilon_{\alpha} n_{\alpha}^{2}, \\
& N(\boldsymbol{n})=\sum_{\alpha} n_{\alpha} . \tag{189}
\end{align*}
$$

(i) Consider a grand canonical ensemble with inverse-temperature $\beta=1 / T$ and chemical potential $\mu$, derive the average particle number $\left\langle n_{\alpha}\right\rangle$ for every the single-particle state $|\alpha\rangle$.
(ii) Discuss the behavior of $\left\langle n_{\alpha}\right\rangle$ as a function of $\epsilon_{\alpha}$ in the low temperature limit as $T \rightarrow 0$.
(iii) Assuming the density of state is given by the following general form

$$
\begin{equation*}
g(\epsilon)=\frac{\Delta \epsilon^{\Delta-1}}{\epsilon_{0}^{\Delta}}, \tag{190}
\end{equation*}
$$

with some typical energy scale $\epsilon_{0}$. Compute the average energy $E$ and average particle number $N$ in the $T \rightarrow 0$ limit as a function of the chemical potential $\mu$.
(iv) Use the above result to express $E$ as a function of $N$ in the $T \rightarrow 0$ limit by eliminating $\mu$.

## - Nondimentionalization

We often encounter complicated integrations (originated from state summation) in calculating thermodynamic quantities. In many cases, these integrations can not be computed analytically. Nondimentionalization is the trick to circumvent the evaluation of these integrals while still giving us useful results.

- Rule 1: the argument of a transcendental function must be dimensionless.
- Examples of transcendental functions: exp, log, trigonometric functions (cos, $\sin , \tan , \ldots$, cosh, sinh, tanh, ...).
- This is because things like $\exp (5$ Joule) does not make sense.
- Rule 2: perform a change of the integration variable to make it dimensionless.

Consider an definite integral of the form

$$
\begin{equation*}
I=\int_{0}^{\infty} d \epsilon \epsilon^{s} f(\beta \epsilon) \tag{191}
\end{equation*}
$$

where $f(\square)$ is a transcendental function. Using the rules, we introduce $x=\beta \epsilon$ as a dimensionless variable, such that $\epsilon=x / \beta$ and

$$
\begin{equation*}
I=\frac{1}{\beta^{s+1}} \int_{0}^{\infty} d x x^{s} f(x) \tag{192}
\end{equation*}
$$

Now the integration has become dimensionless, and simply evaluates to a number (assuming it converges), which allows us to conclude that

$$
\begin{equation*}
I \propto \frac{1}{\beta^{s+1}} . \tag{193}
\end{equation*}
$$

## - Quantum Gas

## - Grand Canonical Ensemble

- The microstate of a quantum gas is described by a collection of occupation numbers

$$
\begin{equation*}
\boldsymbol{n}:=\left\{n_{\alpha} \mid \alpha=1,2, \ldots\right\} . \tag{194}
\end{equation*}
$$

- Energy and particle number for a specific collection $\boldsymbol{n}$

$$
\begin{equation*}
E(\boldsymbol{n})=\sum_{\alpha} \epsilon_{\alpha} n_{\alpha}, N(\boldsymbol{n})=\sum_{\alpha} n_{\alpha} \tag{195}
\end{equation*}
$$

- Probability distribution

$$
\begin{equation*}
p(\boldsymbol{n})=\frac{1}{\mathfrak{Z}} e^{-\beta(E(\boldsymbol{n})-\mu N(\boldsymbol{n}))} \tag{196}
\end{equation*}
$$

and the partition function

$$
\begin{equation*}
\mathcal{Z}=\sum_{n} e^{-\beta(E(n)-\mu N(n))} \tag{197}
\end{equation*}
$$

## - Bosons and Fermions

- Introduce the fermion sign

$$
\eta= \begin{cases}+1 & \text { bosons }  \tag{198}\\ -1 & \text { fermions. }\end{cases}
$$

- Partition function $\mathcal{Z}=\prod_{\alpha} \mathcal{Z}_{\alpha}$, with

$$
\begin{equation*}
\log \boldsymbol{Z}_{\alpha}=-\eta \log \left(1-\eta e^{-\beta\left(\epsilon_{\alpha}-\mu\right)}\right) . \tag{199}
\end{equation*}
$$

- Average occupation number

$$
\begin{equation*}
\left\langle n_{\alpha}\right\rangle=\frac{1}{\boldsymbol{e}^{\beta\left(\epsilon_{a}-\mu\right)}-\eta} . \tag{200}
\end{equation*}
$$

## - Density of State

- Definition

$$
\begin{equation*}
\forall f: \sum_{\alpha} f\left(\epsilon_{\alpha}\right)=V \int d \epsilon g(\epsilon) f(\epsilon) . \tag{201}
\end{equation*}
$$

- General form

$$
\begin{equation*}
g(\epsilon)=\frac{\Delta \epsilon^{\Delta-1}}{\epsilon_{0}^{\Delta}} \tag{202}
\end{equation*}
$$

with

$$
\begin{equation*}
\Delta=\frac{D}{\zeta} \tag{203}
\end{equation*}
$$

- $D$ - dimension of space,
- $\zeta$ - dynamical exponent $\left(\epsilon_{k} \sim k^{\zeta}\right)$.


## - Thermodynamics

- Introduce fugacity

$$
\begin{equation*}
z=e^{\beta \mu}=e^{\mu / T} . \tag{204}
\end{equation*}
$$

- Free energy $\mathcal{F}=-T \log \mathcal{Z}$,

$$
\begin{equation*}
\mathcal{F}=-T V\left(\frac{T}{\epsilon_{0}}\right)^{\Delta} \mathcal{I}_{\eta}^{\Delta+1}(z) \tag{205}
\end{equation*}
$$

- Pressure

$$
\begin{equation*}
P=-\left(\frac{\partial \mathcal{F}}{\partial V}\right)_{T, \mu}=T\left(\frac{T}{\epsilon_{0}}\right)^{\Delta} \mathcal{I}_{\eta}^{\Delta+1}(z) \tag{206}
\end{equation*}
$$

- Entropy

$$
\begin{equation*}
S=-\left(\frac{\partial \mathcal{F}}{\partial T}\right)_{V, \mu}=V\left(\frac{T}{\epsilon_{0}}\right)^{\Delta}\left((\Delta+1) \mathcal{I}_{\eta}^{\Delta+1}(z)-\frac{\Delta \mu}{T} \mathcal{I}_{\eta}^{\Delta}(z)\right) \tag{207}
\end{equation*}
$$

- Particle number

$$
\begin{equation*}
N=-\left(\frac{\partial \mathcal{F}}{\partial \mu}\right)_{V, T}=\Delta V\left(\frac{T}{\epsilon_{0}}\right)^{\Delta} I_{\eta}^{\Delta}(z) \tag{208}
\end{equation*}
$$

- Energy

$$
\begin{align*}
& E=\mathcal{F}+T S+\mu N \\
& =\Delta T V\left(\frac{T}{\epsilon_{0}}\right)^{\Delta} \mathcal{I}_{\eta}^{\Delta+1}(z)  \tag{209}\\
& =\Delta P V
\end{align*}
$$

- Equation of state

$$
\begin{equation*}
P V=\frac{I_{\eta}^{\Delta+1}(z)}{\Delta I_{\eta}^{\Delta}(z)} N T \tag{210}
\end{equation*}
$$

- Higher order properties
- Specific heats

$$
\begin{align*}
& c_{V}=\frac{T}{N}\left(\frac{\partial S}{\partial T}\right)_{N, V} \\
& c_{P}=\frac{T}{N}\left(\frac{\partial S}{\partial T}\right)_{N, P} \tag{211}
\end{align*}
$$

- Susceptibilities

$$
\begin{align*}
& \chi_{N}=\frac{1}{N}\left(\frac{\partial N}{\partial \mu}\right)_{V, T}, \\
& \chi_{Q}=\frac{1}{N}\left(\frac{\partial Q}{\partial \mathcal{E}}\right)_{V, T}=e^{2} \chi_{N}, \tag{212}
\end{align*}
$$

$$
\chi_{M}=\frac{1}{N}\left(\frac{\partial M}{\partial B}\right)_{V, T}=\mu_{B}^{2} \chi_{N} .
$$

## - Special Cases

- $z \rightarrow 0$ : Dilute (classical) limit
- Equation of state

$$
\begin{equation*}
P V=N T \tag{213}
\end{equation*}
$$

- Energy

$$
\begin{equation*}
E=\Delta P V=\Delta N T \tag{214}
\end{equation*}
$$

- Specific heats

$$
\begin{align*}
& c_{V}=\Delta \\
& c_{P}=\Delta+1 \tag{215}
\end{align*}
$$

- $z \rightarrow 1, \eta=+1$ : Bose-Einstein condensation (BEC)
- Condensed fractions

$$
\begin{equation*}
\frac{N_{0}}{N}=1-\left(\frac{T}{T_{c}}\right)^{\Delta} \tag{216}
\end{equation*}
$$

- Transition temperature

$$
T_{c}=\left\{\begin{array}{ll}
\epsilon_{0}\left(\frac{1}{\Gamma(\Delta+1) \zeta(\Delta)} \frac{N}{V}\right)^{1 / \Delta} & \Delta>1  \tag{217}\\
0 & \Delta \leq 1
\end{array} .\right.
$$

- $z=1, \eta=+1$ : Black-body radiation or in the BEC phase
- Equation of state

$$
\begin{equation*}
P V=\frac{\zeta(\Delta+1)}{\zeta(\Delta)} N T \tag{218}
\end{equation*}
$$

- Energy

$$
\begin{equation*}
E=\Delta \kappa V T^{\Delta+1} \tag{219}
\end{equation*}
$$

- Specific heats
$c_{V}=\left(1+\frac{1}{\Delta}\right) \kappa T^{\Delta}$.
- $z \rightarrow \infty, \eta=-1$ : Degenerated fermi gas
- Fermi energy
- Definition $\epsilon_{F}=\mu(T=0)$,
- Formula

$$
\begin{equation*}
\epsilon_{F}=\epsilon_{0}\left(\frac{N}{V}\right)^{1 / \Delta} . \tag{221}
\end{equation*}
$$

- Equation of state $\left(T \ll \epsilon_{F}\right)$

$$
\begin{equation*}
P V=\frac{1}{\Delta+1} N \epsilon_{F} . \tag{222}
\end{equation*}
$$

- Energy $\left(T \ll \epsilon_{F}\right)$

$$
\begin{equation*}
E=\frac{\Delta}{\Delta+1} N \epsilon_{F} . \tag{223}
\end{equation*}
$$

- Specific heats $\left(T \ll \epsilon_{F}\right)$

$$
\begin{equation*}
c_{V}=\frac{\pi^{2} \Delta}{3}\left(\frac{T}{\epsilon_{F}}\right) \tag{224}
\end{equation*}
$$

- Susceptibilities $\left(T \ll \epsilon_{F}\right)$

$$
\begin{align*}
& \chi_{N}=\frac{\Delta}{\epsilon_{F}}, \\
& \chi_{Q}=\frac{\Delta e^{2}}{\epsilon_{F}},  \tag{225}\\
& \chi_{M}=\frac{\Delta \mu_{B}^{2}}{\epsilon_{F}} .
\end{align*}
$$


[^0]:    Exc
    22

