Part VI

- The Grand Partition Function $Q(T,V,\mu)$
- General Formalism based on $Q(T,V,\mu)$
- $Q(T,V,\mu)$ can be evaluated exactly for non-interacting fermions and bosons
- Re-deriving Fermi-Dirac and Bose-Einstein distributions
- General sets of equations for studying ideal Fermi Gas and ideal Bose Gas

XI. Systems with Variable particle numbers

▪ The Gibbs distribution and Grand Canonical Ensemble

Motivations

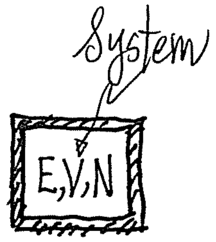
▪ For macroscopic systems, the thermodynamics (the physics) should not depend on we treat the problems.

We have seen the same physics results in, e.g. 2-level systems and collection of harmonic oscillators, by working within the microcanonical ensemble theory

$[W(E,V,N) \to S = k\ln W \to$ other variables$]$

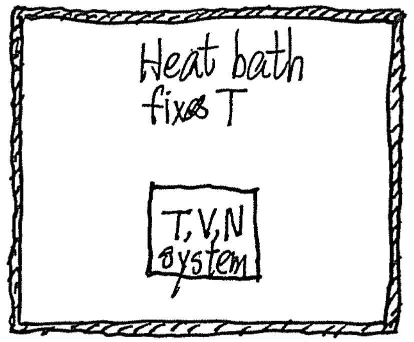
and the canonical ensemble theory

$[Z(T,V,N) \to F = -kT\ln Z \to$ other variables$]$



Microcanonical Ensemble

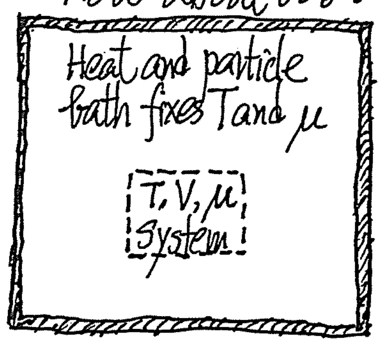
Get W(E,V,N) and everything follows



Canonical Ensemble

Get Z(T,V,N) and everything follows

How about...?



Grand Canonical Ensemble

Get Q(T,V,μ) and everything follows!

What is Q(T,V,μ)?

▪ Z(T,V,N) is hard to evaluate for fermions/bosons even when they are non-interacting.

Recall (see Ch. VI)

VI-(80)

Partition Function Z

\# particle in single-particle state r

- In a state specified by $\{n_1, n_2, \ldots, n_r, \ldots\}$, the energy is $E(\{n_1, n_2, \ldots\}) = \sum_r n_r \varepsilon_r$

- We have $\sum_r n_r = N$ —— (a)
- We have $\begin{cases} n_r = 0 \text{ or } 1 & \text{for fermions — (b)} \\ n_r = 0,1,2,3,\ldots & \text{for bosons — (c)} \end{cases}$

This requirement makes Z(T,V,N) hard to evaluate

$$Z(T,V,N) = \sum_{\text{allowed }\{n_r\}} e^{-\beta\left(\sum_r \varepsilon_r n_r\right)} = \sum_{\text{allowed }\{n_r\}} e^{-\beta(n_1\varepsilon_1 + n_2\varepsilon_2 + \cdots + n_r\varepsilon_r + \cdots)}$$

Important: $\sum_{\text{allowed }\{n_r\}}$ is a sum over all sets of $\{n_i\}$ satisfying

$\begin{cases} \text{(a) AND (b) for fermions} \\ \text{(a) AND (c) for bosons} \end{cases}$

Note: If the requirement is (b) only or (c) only, it will be easy to do the sum. But [(a) AND (b)], [(a) AND (c)] make the calculation of Z hard to do!

▪ The Grand Canonical Ensemble approach simplifies the calculation.

▪ In some cases not dealing with "real" (matter) particles in which N is not fixed, Z can be calculated.

∴ Need to find a way out by relaxing the requirement $\sum_r n_r = N$, i.e. consider systems in which N is not fixed but may vary. Nonetheless, there is a good mean number $\langle N\rangle$.

VI-(81)

Ideal Fermi/Bose Gases

Z is not easy to get!

Ways out?

short cut ↓ Go back to microcanonical ensemble (E, V, N) and look for most probable distributions for fermions/bosons

Physics is physics!

The same physics results!

- Fermi-Dirac distribution
- Bose-Einstein distribution

Did this in Ch. VII and Ch. VIII

new formalism ↓ Grand Canonical Ensemble

Idea: Z is hard to get because of the "$\sum_r n_r = N$" requirement in listing out the states.

How about relaxing the requirement?

We develop this new formalism in this Chapter

Recall: We know that for non-interacting fermions/bosons:

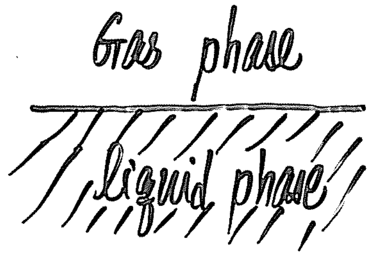
$$N = \sum_{\text{all s.p. states } i} \frac{1}{e^{\beta(\varepsilon_i-\mu)}\pm 1} = \sum_{\substack{\text{all levels } r\\ \text{(cells)}}} g_r \frac{1}{e^{\beta(\varepsilon_r-\mu)}\pm 1}$$

and

$$E = \sum_{\text{all s.p. states } i} \frac{\varepsilon_i}{e^{\beta(\varepsilon_i-\mu)}\pm 1} = \underbrace{\sum_{\text{all levels } r} g_r \frac{\varepsilon_r}{e^{\beta(\varepsilon_r-\mu)}\pm 1}}_{\text{can turn into integrals using the single-particle density of states } g(\varepsilon)d\varepsilon}$$

- In addition to analytical convenience, there are real situations in which the particle number varies.

e.g.



$N_{gas} + N_{liq.} = $ Total # atoms

vary ↑ ↑ ; fixed ⇑

$(dN_{gas} = -dN_{liq})$

e.g. chemical reactions

$$A + B \rightleftharpoons \underset{\text{AB molecule}}{AB}$$

Total # A atoms $= N_A + N_{AB} =$ constant (N_A, N_{AB} vary)

$(dN_A = -dN_{AB})$

Total # B atoms $= N_B + N_{AB} =$ constant (N_B, N_{AB} vary)

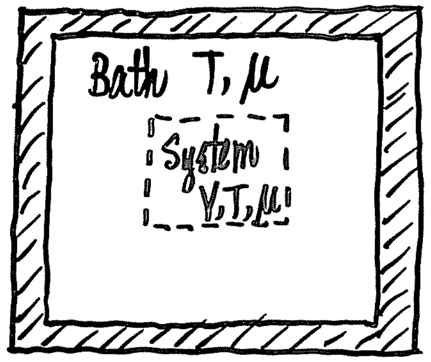
$(dN_B = -dN_{AB})$

$(dN_A = dN_B)$

∴ A formalism with varying particle number will also be useful in studying chemical/nuclear reactions.

A. The Gibbs Distribution

- Consider a system in thermal contact and diffusive contact with a bath ← heat bath and particle bath

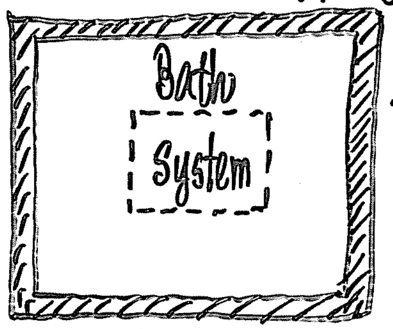


Key features

T, V, μ fixed

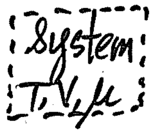
E, N fluctuate (⟨E⟩, ⟨N⟩ sharp)

- System and bath can exchange energy AND exchange particles
- Wait and wait : system in equilibrium with bath
  ⇒ fixed T, V, μ
- Bath is huge
  - control T and μ
  - bath is so large that energy exchange and particle exchange do NOT affect T and μ of the bath



← form an isolated system

Consider the physics of



The Key Question:

What is the probability of finding the system in a state of N particles of energy $E_i(N)$, when the system is in equilibrium with a bath at temperature T and chemical potential μ?

The Key Result:

For a state with N particles and of energy $E_i(N)$, the probability $P(E_i(N), N)^{\dagger}$ of finding the system in such a state when the system is in equilibrium with a bath at temperature T and chemical potential μ is:

$$P(E_i(N), N) \propto e^{-\beta E_i(N) + \beta\mu N}$$

- Gibbs distribution or grand canonical distribution

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† The simplest notation may be $P_{N,i}$.

- <u>Understanding the Question</u>
  - Number of particles is varying

At one moment, $N = N_1$ (say)

$$\hat{H}_{N_1}\psi(\vec{r}_1,\vec{r}_2,\cdots,\vec{r}_{N_1}) = E(N_1)\,\psi(\vec{r}_1,\vec{r}_2,\cdots,\vec{r}_{N_1})$$

N_1-particle System

Solve the Schrödinger Equation (which is not an easy task)

<u>energy</u>	<u>states</u>	<u>degeneracy</u>
$\vdots$	$\vdots$	$\vdots$
$E_4(N_1)$	$\psi^{(1)}_{E_4(N_1)}, \psi^{(2)}_{E_4(N_1)}, \cdots, \psi^{W_s(E_4,N_1)}_{E_4(N_1)}$	$W_s(E_4,N_1,V)$
$E_3(N_1)$	$\vdots$	$\vdots$
$E_2(N_1)$		
$E_1(N_1)$	$\underbrace{\psi^{(1)}_{E_1(N_1)}, \psi^{(2)}_{E_1(N_1)}, \cdots, \psi^{W_s(E_1,N_1)}_{E_1(N_1)}}$	$W_s(E_1,N_1,V)$

allowed energy levels of N_1-particle system

possible to have degenerate eigenstates

↪ $W_s(E_i, N_1, V)$ of them with eigen-energy $E_i(N_1)$

"system"

But all these are about N_1 only!

At another moment, $N = N_2$ (different from N_1)

$$\hat{H}_{N_2}\psi(\vec{r}_1,\cdots,\vec{r}_{N_2}) = E(N_2)\,\psi(\vec{r}_1,\cdots,\vec{r}_{N_2})$$

N_2-particle system

- Another QM problem
- Solve the Schrödinger Equation

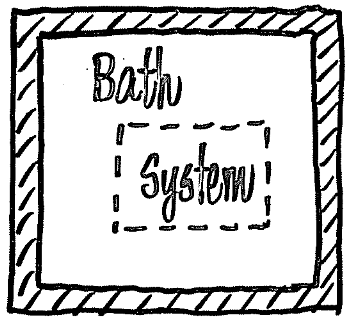
<u>energy</u>	<u>states</u>	<u>degeneracy</u>
$\vdots$	$\vdots$	$\vdots$
$E_4(N_2)$	$\psi^{(1)}_{E_4(N_2)}, \psi^{(2)}_{E_4(N_2)}, \cdots, \psi^{W_s(E_4,N_2)}_{E_4(N_2)}$	$W_s(E_4,N_2,V)$
$E_3(N_2)$	$\vdots$	$\vdots$
$E_2(N_2)$		
$E_1(N_2)$	$\psi^{(1)}_{E_1(N_2)}, \psi^{(2)}_{E_1(N_2)}, \cdots, \psi^{W_s(E_1,N_2)}_{E_1(N_2)}$	$W_s(E_1,N_2,V)$

<u>Note:</u> $\{E_i(N_1)\} \neq \{E_i(N_2)\}$ as they are solutions to <u>two different</u> QM problems

<u>Our question is:</u>

Prob. of finding the system in <u>a state</u> of N particles with energy $E_i(N)$?

Gibbs distribution - Derivation



- Whole (bath + system) system is an isolated system
  (N_0, E_0, V_0) fixed

$$\boxed{\begin{array}{l} \underset{\uparrow\ \text{fixed}}{N_0} = \underbrace{N_B + N}_{\underline{\text{not}}\ \text{fixed}} \leftarrow \text{in system} \\ E_0 = \underbrace{E_B + E_i(N)}_{\underline{\text{not}}\ \text{fixed}} \end{array}}\ ; \quad V_0 = \underbrace{V_B + V}_{\substack{\text{fixed}\\ \text{(no exchange of}\\ \text{volume)}}}$$

- When the whole composite (bath + system) system reaches equilibrium, we have <u>equal a priori probabilities</u>

$\Downarrow$

<u>every microstate is equally probable</u>

∴ Prob. of finding the system to have N particles and in an <u>energy level</u> $E_i(N)$

(Important: <u>NOT</u> a state!)

$$= \frac{W_B(E_0-E_i(N), N_0-N, V_B)\cdot W_S(E_i(N), N, V)}{W}$$

W: { total # of accessible state of composite system for given (E_0, N_0, V_0)

→ this is just a number (constant)

∴ Prob. of finding the system in <u>a state</u> of N particles with energy $E_i(N)$

$$= P(E_i(N), N) \propto W_B(E_0-E_i(N), N_0-N)$$

- Next, we want to get $W_B(E_0-E_i(N), N_0-N)$
- Since $E_i(N) \ll E_0$, $N \ll N_0$ (hugh bath), we expand $\ln W_B(E_0-E_i(N), N_0-N)$ about (E_0, N_0)

$$\ln W_B(E_0-E_i(N), N_0-N)$$

$$\approx \underbrace{\ln W_B(E_0,N_0)}_{\text{some number}} - E_i(N)\underbrace{\left(\frac{\partial \ln W_B(E,M)}{\partial E}\right)_{E=E_0, M=N_0}}_{\substack{\frac{1}{kT}\\ T=\text{temp. of } \underline{\text{bath}}}} - N\underbrace{\left(\frac{\partial \ln W_B(E,M)}{\partial M}\right)_{\substack{E=E_0\\ M=N_0}}}_{\substack{-\frac{\mu}{kT}\\ \mu = \text{chemical potential}\\ \text{of bath}}}$$

$$\approx \ln W_B(E_0,N_0) - \frac{E_i(N)}{kT} + \frac{\mu N}{kT}$$

$$\therefore\ W_B(E_0-E_i(N), N_0-N) = \underbrace{W_B(E_0,N_0)}_{\text{just a number}}\, e^{-\frac{E_i(N)}{kT} + \frac{\mu N}{kT}}$$

$$\therefore\ P(E_i(N),N) \propto e^{-\frac{E_i(N)}{kT}+\frac{\mu N}{kT}} = e^{-\beta E_i(N)+\beta\mu N}$$

recall: talking about a state

Gibbs factor

Normalization:

$$P(E_i(N),N) \propto e^{-\beta E_i(N)+\beta\mu N} = C\,e^{-\beta E_i(N)+\beta\mu N}$$

$$\sum_{\text{all states of the system}} P(E_i(N),N) = 1 \qquad \text{(normalization condition)}$$

Meaning: $N=0,1,2,\dots$
and for given N, all states i

now "i" labels the states $\psi_N^{(i)}$ with energy $E_i(N)$

$$\therefore\ C\sum_{N=0}^{\infty}\sum_{i} e^{-\beta E_i(N)+\beta\mu N} = 1$$

over possible values of N

all N-particle states i

$$\Rightarrow\ C = \frac{1}{\sum_{N=0}^{\infty}\sum_{i} e^{-\beta E_i(N)+\beta\mu N}} \equiv \frac{1}{Q(T,\mu,V)}$$

Here enters $\boxed{\text{Grand Partition Function}^{\dagger}}$

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†Note: Conceptually, the derivation is the same as that of the Gibbs distribution. The partition function (T,V,N fixed) becomes the grand partition function (T,μ,V fixed.)

$$\boxed{P(E_i(N),N) = \frac{e^{-\beta E_i(N)+\beta\mu N}}{\sum_{N=0}^{\infty}\sum_{i} e^{-\beta E_i(N)+\beta\mu N}} = \frac{1}{Q(T,\mu,V)}\,e^{-\beta(E_i(N)-\mu N)}}$$

all values of N

all N-particle states

- This is the (normalized) Gibbs distribution or the grand canonical distribution

- A huge collection of systems (for fixed T,μ,V) in which the members are selected according to $P(E_i(N),N)$ is called a grand canonical ensemble. A simple average over members in a grand canonical ensemble to get an averaged quantity is the same as averaging the same quantity in one system over time.

- Different books have different notations for the Grand Partition Function. Besides $Q(T,V,\mu)$, $\Xi(T,V,\mu)$ is another popular choice.

Grand Partition Function

$$\boxed{Q(T,\mu,V) \equiv \sum_{N=0}^{\infty}\sum_{i \,\leftarrow\, \text{all } N\text{-particle states } i} e^{-\beta E_i(N)+\beta\mu N}}$$

- $Q(T,\mu,V)$ normalizes $P(E_i(N),N)$
- A generalization of $Z(T,V,N)$ to cases in which the system can exchange particles as well as energy with the bath, i.e., when energy and number of particles are not fixed.
- Like $Z(T,V,N)$, if we know $Q(T,\mu,V)$, all the thermodynamics of the system follows.
- Thus, $W(E,V,N)$ (microcanonical ensemble, E,V,N fixed)
  $Z(T,V,N)$ (canonical ensemble, T,V,N fixed)
  $Q(T,\mu,V)$ (grand canonical ensemble, T,μ,V fixed)
  provide us three calculation schemes.

They should give the same results when we consider the thermodynamics of macroscopic systems.

B. $Q(T,\mu,V)$ and $Z(T,N,V)$

$$Q(T,V,\mu) = \sum_{N=0}^{\infty}\sum_{\substack{\text{all } N\text{-particle}\\ \text{states } i}} e^{-\beta E_i(N)+\beta\mu N}$$

$$= \sum_{N=0}^{\infty} e^{\beta\mu N} \underbrace{\sum_{\substack{\text{all } N\text{-particle}\\ \text{states } i}} e^{-\beta E_i(N)}}_{\text{this is } Z(T,N,V)}$$

$$\therefore \quad \boxed{Q(T,V,\mu) = \sum_{N=0}^{\infty} e^{\beta\mu N} Z(T,V,N)}$$

- The quantity $e^{\beta\mu}$ (note: without the "N" in the exponent) is called the fugacity or absolute activity, ξ.
- For the mathematically inclined students, you may have noticed that $Q(T,V,\mu)$ "generates" $Z(T,V,N)$, or $Q(T,V,\mu)$ is a generating function.

$$Q(T,V,\mu) = \sum_{N=0}^{\infty} \underset{\substack{\uparrow\\ \text{absolute activity or fugacity}}}{\xi}{}^{N}\, Z(T,V,N)$$

Remarks:

(a) We saw $$\underset{\substack{\uparrow \\ \text{grand partition function}}}{Q(T,V,\mu)} = \sum_{N=0}^{\infty} e^{\beta\mu N} \underbrace{Z(T,V,N)}_{\text{partition function}}$$

There is an analogous relation between $Z(T,V,N)$ and $W(E,V,N)$.

$$\underset{\substack{\uparrow \\ \text{canonical} \\ \text{ensemble}}}{Z(T,V,N)} = \sum_{\substack{\text{all N-particle} \\ \text{states } i}} e^{-\beta E_i} = \sum_{\substack{\text{all different} \\ \text{energy levels } E}} \overbrace{W(E,V,N)}^{\substack{\text{microcanonical} \\ \text{ensemble}}} e^{-\beta E}$$

$$= \int \mathcal{W}(E,V,N)\, e^{-\beta E}\, dE \quad \text{in integral form}$$

where $\mathcal{W}(E,V,N)dE$ = # N-particle states with energy in interval $E \to E+dE$

$W(E,V,N)$ or $\mathcal{W}(E,V,N)\,dE$ can be used to evaluate the entropy $S(E,V,N)$ [microcanonical ensemble]

(b) Then, why bother?

Sometimes, easier to get $Z(T,V,N)$ than $W(E,V,N)$.

Similarly, sometimes it is easier to get $Q(T,V,\mu)$ than $Z(T,V,N)$.

(c) $$Q(T,V,\mu) = \sum_{N=0}^{\infty} e^{\beta\mu N} Z(T,V,N) \equiv \sum_{N=0}^{\infty} \xi^N Z(T,V,N)$$

The "ξ" $= e^{\beta\mu} = e^{\frac{\mu}{kT}}$ does not look familiar!

Not quite! You saw this quantity for the classical ideal gas (see Ch. IV, Appendix B).

Using $$S = Nk \ln\left[\left(\frac{V}{N}\right)\left(\frac{\sqrt{2\pi mkT}}{h}\right)^3\right] + \frac{5}{2}Nk$$ Sacker-Tetrode Equation

$$\frac{\mu}{T} = -\frac{\partial S}{\partial N}$$

$$\Rightarrow \underset{\uparrow}{\mu} = -kT \ln\left[\left(\frac{V}{N}\right)\left(\frac{\sqrt{2\pi mkT}}{h}\right)^3\right]$$

thus μ is negative for classical ideal gas

$$\xi = e^{\frac{\mu}{kT}} = e^{\ln\left[\left(\frac{V}{N}\right)^{-1}\left(\frac{\sqrt{2\pi mkT}}{h}\right)^{-3}\right]}$$

$$= \frac{1}{\left(\frac{V}{N}\right)\left(\frac{\sqrt{2\pi mkT}}{h}\right)^3} = \frac{\lambda_{th}^3}{\left(\frac{V}{N}\right)}$$

$$\boxed{\therefore \text{ For classical ideal gas, } \xi = \frac{\lambda_{th}^3(T)}{\underset{\uparrow}{\left(\frac{V}{N}\right)}} \ll 1}$$

ratio of λ_{th}^3 and $\left(\frac{\text{Volume}}{\text{Particle}}\right)$, thus how unimportant quantum effect is.

C. Mean number of Particles / Fluctuations in particle number

- Quick applications of Gibbs distribution

- Since N fluctuates, we can consider the mean number of particles ⟨N⟩ in the system and its fluctuations.

$$\langle N\rangle = \sum_{N=0}^{\infty}\sum_i N\, P(E_i(N), N)$$

(Meaning of stat. mech. average)

$$= \frac{1}{Q}\sum_{N=0}^{\infty}\sum_i N\, e^{-\beta E_i(N)+\beta\mu N}$$

$$= \frac{1}{Q}\frac{1}{\beta}\left(\frac{\partial}{\partial\mu}\Big\{\underbrace{\sum_{N=0}^{\infty}\sum_i e^{-\beta E_i(N)+\beta\mu N}}_{Q(T,\mu,V)}\Big\}\right)_{T,V}$$

$$= \frac{1}{Q}\frac{1}{\beta}\left(\frac{\partial Q}{\partial\mu}\right)_{T,V}$$

$$= \frac{1}{\beta}\left(\frac{\partial}{\partial\mu}\ln Q\right)_{T,V} = kT\left(\frac{\partial}{\partial\mu}\ln Q\right)_{T,V}$$

$$\therefore \boxed{\langle N\rangle = \frac{1}{\beta}\left(\frac{\partial \ln Q}{\partial\mu}\right)_{T,V}} \leftarrow \text{formula giving } \langle N\rangle \text{ from } Q$$

↳ Note: $\langle N\rangle = \langle N\rangle(T,\mu,V)$ since $Q(T,\mu,V)$

Fluctuations in Particle numbers

$$\langle(\Delta N)^2\rangle = \langle(N-\langle N\rangle)^2\rangle = \langle N^2\rangle - \langle N\rangle^2$$

$$\langle N\rangle = \frac{1}{\beta}\frac{1}{Q}\left(\frac{\partial Q}{\partial\mu}\right)_{T,V}$$

Need $\langle N^2\rangle$

$$\langle N^2\rangle = \frac{1}{Q}\sum_{N=0}^{\infty}\sum_i N^2 e^{-\beta E_i(N)+\beta\mu N}$$

$$= \frac{1}{Q}\frac{1}{\beta^2}\left(\frac{\partial^2 Q}{\partial\mu^2}\right)_{T,V}$$

$$\langle(\Delta N)^2\rangle = \frac{1}{\beta^2}\left[\frac{1}{Q}\frac{\partial^2 Q}{\partial\mu^2} - \frac{1}{Q^2}\left(\frac{\partial Q}{\partial\mu}\right)^2\right]$$

$$= \frac{1}{\beta^2}\frac{\partial}{\partial\mu}\left(\frac{1}{Q}\frac{\partial Q}{\partial\mu}\right) = \frac{1}{\beta}\frac{\partial\langle N\rangle}{\partial\mu} = \frac{1}{\beta^2}\frac{\partial^2\ln Q}{\partial\mu^2}$$

$$\therefore \boxed{\langle(\Delta N)^2\rangle = kT\left(\frac{\partial\langle N\rangle}{\partial\mu}\right)_{T,V}} = \frac{kT\langle N\rangle^2\kappa}{V}^{+}$$

Relative fluctuation in particle number:

$$\boxed{\frac{\sqrt{\langle(\Delta N)^2\rangle}}{\langle N\rangle} = \sqrt{\frac{kT}{\langle N\rangle^2}\left(\frac{\partial\langle N\rangle}{\partial\mu}\right)_{T,V}}}$$

+ Since $\left(\frac{\partial\mu}{\partial N}\right)_{V,T} = -\frac{V^2}{N^2}\left(\frac{\partial p}{\partial V}\right)_{N,T}$ and $-\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_{N,T} \equiv K_T$ is the isothermal compressibility.

The point is:

$$\langle(\Delta N)^2\rangle = \underset{\text{intensive}}{kT}\left(\frac{\partial\overset{\text{extensive}}{\langle N\rangle}}{\underset{\text{intensive}}{\partial\mu}}\right)_{T,V} = kT\,\frac{\overbrace{\langle N\rangle}^{\text{extensive}}{}^{2}}{V}\,\kappa \quad \leftarrow \text{intensive}$$

$\langle(\Delta N)^2\rangle$ is extensive and $\sim \langle N\rangle$

$$\therefore \frac{\sqrt{\langle(\Delta N)^2\rangle}}{\langle N\rangle} \sim \frac{\sqrt{\langle N\rangle}}{\langle N\rangle} \sim \frac{1}{\sqrt{\langle N\rangle}}$$

$\therefore$ $\langle N\rangle$ is highly representative and it plays the role of N in thermodynamics

Remark:

Recall: $\langle(\Delta E)^2\rangle = \underset{\text{intensive}}{kT^2}\left(\frac{\partial\overset{\text{extensive}}{\langle E\rangle}}{\underset{\text{intensive}}{\partial T}}\right)_{N,V}$ in canonical ensemble

which is analogous to

$$\langle(\Delta N)^2\rangle = kT\left(\frac{\partial\langle N\rangle}{\partial\mu}\right)_{T,V}$$ above.

D. Mean Energy $\langle E\rangle$ or U or simply E

- The system does not have fixed energy

$\Rightarrow$ energy fluctuates

We consider the mean energy $\langle E\rangle$ or U ← in thermodynamics notations

$$U = \langle E\rangle = \sum_{N=0}^{\infty}\sum_{\substack{\text{all } N\text{-particle}\\ \text{states } i}} E_i(N)\,P(E_i(N),N)$$ [Meaning of stat. mech. average]

$$= \sum_{N=0}^{\infty}\sum_{i} E_i(N)\,\frac{1}{Q}\,e^{-\beta E_i(N)+\beta\mu N}$$

Consider

$$\left(\frac{\partial}{\partial\beta}\ln Q\right)_{\mu,V} = \frac{1}{Q}\left(\frac{\partial Q}{\partial\beta}\right)_{\mu,V}$$

$$= \frac{1}{Q}\frac{\partial}{\partial\beta}\left(\sum_{N=0}^{\infty}\sum_{i} e^{-\beta E_i(N)+\beta\mu N}\right)$$

$$= \frac{1}{Q}\sum_{N=0}^{\infty}\sum_{i}\left(\mu N - E_i(N)\right)e^{-\beta E_i(N)+\beta\mu N}$$

$$= \mu\langle N\rangle - \langle E\rangle$$

$$\therefore \boxed{U = \langle E\rangle = \mu\langle N\rangle - \left(\frac{\partial\ln Q}{\partial\beta}\right)_{\mu,V}}$$ ← Formula giving $\langle E\rangle$ or U from Q

Recall: $\langle N\rangle = \frac{1}{\beta}\left(\frac{\partial\ln Q}{\partial\mu}\right)_{T,V}$

Again, the point is:

Although formally, we talk about mean energy $\langle E\rangle$ and mean particle number $\langle N\rangle$ of the system, but for macroscopic systems, $\langle E\rangle$ and $\langle N\rangle$ are very sharp! Thus $\langle E\rangle$ plays the role of E (or U) and $\langle N\rangle$ plays the role of N in thermodynamics.

E. Connecting Gibbs distribution to thermodynamics

Key Result:

$$\boxed{\underbrace{\Omega(T,V,\mu)}_{\text{Grand Potential}} = -kT\ln \underbrace{Q(T,V,\mu)}_{\text{Grand Partition Function}}}$$

- There are many ways to establish this result
- Collect what we know so far...

$$\langle N\rangle = \frac{1}{\beta}\left(\frac{\partial \ln Q}{\partial \mu}\right)_{T,V} = -\left(\frac{\partial[-kT\ln Q]}{\partial\mu}\right)_{T,V} \qquad (1)$$

$$\langle E\rangle - \mu\langle N\rangle = -\left(\frac{\partial}{\partial\beta}\ln Q\right)_{\mu,V} \qquad (2)$$

「 Consider $\left[\frac{\partial}{\partial\beta}\left(-\frac{1}{\beta}\ln Q\right)\right]_{\mu,V}$

$$= -\frac{1}{\beta}\frac{\partial}{\partial\beta}\ln Q + \frac{1}{\beta^2}\ln Q$$

$$\therefore \underbrace{-\frac{\partial}{\partial\beta}\ln Q}_{\text{appears in (2)}} = \beta\frac{\partial}{\partial\beta}\left(-\frac{1}{\beta}\ln Q\right) - \frac{1}{\beta}\ln Q$$

$$\therefore \underbrace{-\frac{\partial}{\partial\beta}\ln Q}_{\text{appears in (2)}} = \frac{-kT^2}{kT}\frac{\partial}{\partial T}\left[-kT\ln Q\right] - kT\ln Q$$

$$= -T\frac{\partial}{\partial T}\left[-kT\ln Q\right] - kT\ln Q$$

Eq. (2) can be rewritten as:

$$\boxed{\langle E\rangle - \mu\langle N\rangle + T\frac{\partial}{\partial T}\left[-kT\ln Q\right] = -kT\ln Q} \quad (2')$$

Question is:

From thermodynamics, is there a quantity that satisfies the following formulas?

$$\begin{cases} N = -\dfrac{\partial}{\partial\mu}(\text{Something}) \\ E - \mu N + T\dfrac{\partial}{\partial T}(\text{Something}) = (\text{something}) \\ \text{AND that (Something) has } (T, V, \mu) \text{ as variables} \end{cases}$$

What is that "something" in thermodynamics?

A bit of thermodynamics

- We know $dE = TdS - pdV + \mu dN$ $\left\{\begin{array}{l}\text{1st \& 2nd} \\ \text{laws} \\ \text{combined}\end{array}\right.$

  $\therefore E(S, V, N)$

  and $E = TS - pV + \mu N$ (Euler's Equation)

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- We need an energy using (T, V, μ) as variables
- Legendre Transformation

$$E - TS - \mu N \equiv \Omega \leftarrow \boxed{\text{"Grand Potential"}}$$

$$d\Omega = dE - TdS - SdT - \mu dN - Nd\mu$$

$$\Rightarrow \boxed{d\Omega = -SdT - pdV - Nd\mu}$$

$\therefore \Omega = \Omega(T, V, \mu)$ as required

$$S = -\left(\frac{\partial\Omega}{\partial T}\right)_{V,\mu};\quad p = -\left(\frac{\partial\Omega}{\partial V}\right)_{T,\mu};\quad N = -\left(\frac{\partial\Omega}{\partial\mu}\right)_{T,V}$$

$$\therefore E - \mu N + T\frac{\partial\Omega}{\partial T} = \Omega \quad \text{(thermodynamics)}$$

That "something" is $\Omega(T, V, \mu)$!

Comparing with (2'):

$$\boxed{\underset{\substack{\uparrow \\ \text{macroscopic}}}{\Omega(T, V, \mu)} = -kT\ln \underset{\substack{\nwarrow \\ \text{microscopic}}}{Q(T, V, \mu)}}$$

The bridge is:

$$\Omega(T,V,\mu) = -kT\ln Q(T,V,\mu)$$

Using $\Omega(T,V,\mu)$,

$$S = -\left(\frac{\partial\Omega}{\partial T}\right)_{V,\mu} \; ; \; p = -\left(\frac{\partial\Omega}{\partial V}\right)_{T,\mu} \; ; \; N = -\left(\frac{\partial\Omega}{\partial \mu}\right)_{T,V}$$

We have earlier

$$E = \mu N - \left(\frac{\partial \ln Q}{\partial \beta}\right)_{V,\mu}$$

∴ We have a calculation scheme for systems with (T,V,μ), i.e.

Evaluate $Q(T,V,\mu)$ and everything follows!

Remark: Connecting Gibbs distribution to thermodynamics

[An alternative approach]

Recall: General formula for the entropy (Gibbs entropy)

$$S = -k\sum_{N=0}^{\infty}\sum_{\substack{\text{all } N\text{-particle}\\ \text{states } i}} P(E_i(N),N)\,\underbrace{\ln P(E_i(N),N)}$$

$$= -k\sum_{N=0}^{\infty}\sum_{i} P(E_i(N),N)\left[-\beta E_i(N) + \beta\mu N - \ln Q\right]$$

$$= \beta k\left(E - \mu\langle N\rangle\right) + k\ln Q\,\underbrace{\sum_{N=0}^{\infty}\sum_{i} P(E_i(N),N)}_{1 \text{ (normalization)}} \qquad (*)$$

$$\therefore \boxed{S = \frac{E}{T} - \frac{\mu\langle N\rangle}{T} + k\ln Q} \leftarrow \text{formula giving } S(T,\mu,V)$$

Further development:

$$\underbrace{-kT\ln Q}_{\text{some kind of energy or called potential in thermodynamics}} = E - TS - \mu\langle N\rangle \qquad \left(\text{every term is } \underline{\text{extensive}}\right)$$

$$\boxed{\begin{array}{c}\underline{\text{Define the Grand Potential } \Omega = \Omega(T,\mu,V)} \\ \Omega(T,\mu,V) = -kT\ln Q(T,\mu,V) = E - TS - \mu\langle N\rangle\end{array}}$$

(*) Note: Here E is $\langle E\rangle$, but $\langle E\rangle$ is sharp and plays the role of E in thermodynamics.

F. $\underline{\Omega = E - TS - \mu N = -pV}$ <u>provides a short cut to get Equation of State</u>

Euler's Equation: $E = TS - pV + \mu N$

$$\Rightarrow \underbrace{E - TS - \mu N} = -pV$$

$$\boxed{\Omega = -pV}$$

<u>Implications</u>

- <u>Short cut of getting Equation of State</u>

$$\Omega(T,V,\mu) = -kT \ln Q(T,V,\mu)$$

$$\therefore \underbrace{\boxed{pV = kT \ln Q(T,V,\mu)}}_{\text{an equation relating thermodynamic variables (equation of state)}}$$

- A meaning of pressure

$$p = -\frac{\Omega}{V}$$

"pressure is (negative of) grand potential per unit volume"

<u>Remarks</u>:

- Look at $\Omega(\overset{\text{intensive}}{T}, \underset{\uparrow}{V}, \overset{\text{intensive}}{\mu})$

V is the only <u>extensive</u> variable in Ω

Scaling: $\Omega(T,\lambda V,\mu) = \lambda\,\Omega(T,V,\mu)$ ($\because$ Ω is extensive)

Let $\lambda = 1+\epsilon$ ($\epsilon \ll 1$)

$$\underbrace{\Omega(T, V+\epsilon V, \mu)}_{\text{expands}} = (1+\epsilon)\,\Omega(T,V,\mu)$$

$$\Omega(T,V,\mu) + \left(\frac{\partial \Omega}{\partial V}\right)\cdot \epsilon V = \Omega(T,V,\mu) + \epsilon\,\Omega(T,V,\mu)$$

$$\Rightarrow -pV = \Omega \quad \text{as before}$$

$$\underset{\substack{\uparrow \\ \text{variable conjugate} \\ \text{to } V}}{p} = -\frac{\Omega}{\underset{\substack{\uparrow \\ \text{only extensive variable} \\ \text{in } \Omega}}{V}}$$

Further remarks:

An analogous case: $\underbrace{G(\overset{\text{intensive}}{T,p},\ \overset{\text{only extensive variable in } G}{N})}_{\text{Gibbs free energy in thermodynamics}}$

$$\underset{\text{conjugate to } N}{\mu} = \left(\frac{\partial G(T,p,N)}{\partial N}\right)_{T,p}$$

$$G(T,p,\lambda N) = \lambda G(T,p,N)$$

⋮ (same steps)

$$\boxed{\mu N = G(T,p,N)}$$

OR $\underset{\text{conjugate to } N}{\mu} = \dfrac{G(T,p,N)}{\underset{\text{only extensive variable in } G}{N}}$ "μ is the Gibbs free energy per particle"

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We see the chemical potential μ in:

(1) $dE = TdS - pdV + \mu dN \Rightarrow \mu = \left(\frac{\partial E}{\partial N}\right)_{S,V}$ $E(S,V,N)$

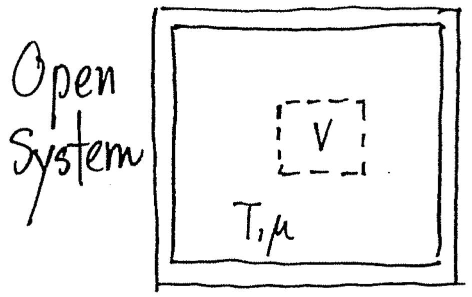
(2) $dS = \frac{1}{T}dE + \frac{p}{T}dV - \frac{\mu}{T}dN \Rightarrow \mu = -T\left(\frac{\partial S}{\partial N}\right)_{E,N}$ $S(E,V,N)$

(3) $dF = -SdT - pdV + \mu dN \Rightarrow \mu = \left(\frac{\partial F}{\partial N}\right)_{T,V}$ $F(T,V,N)$

(4) $G = F + pV = E - TS + pV$

$dG = -SdT + Vdp + \mu dN \Rightarrow \mu = \left(\frac{\partial G}{\partial N}\right)_{T,p}$ $G(T,p,\overset{\text{only extensive}}{N})$

Summary



$$P(E_i(N),N) = \frac{e^{-\beta E_i(N)+\beta\mu N}}{Q(T,\mu,V)}$$ Gibbs distribution

$$\underset{\text{Grand Partition Function}}{Q(T,\mu,V)} = \sum_{N=0}^{\infty}\ \sum_{N\text{-particle states } i} e^{-\beta E_i(N)+\beta\mu N}$$

(T,V,μ) fixed

E and N fluctuate

$$\underset{\text{Grand potential}}{\Omega(T,\mu,V)} = -kT\ln Q(T,\mu,V)$$ [bridge between macroscopic and microscopic descriptions]

$$d\Omega = -SdT - Nd\mu - pdV$$

$$\langle N\rangle = -\frac{\partial\Omega}{\partial\mu} = \frac{1}{\beta}\frac{\partial\ln Q}{\partial\mu}$$

$$S = -\frac{\partial\Omega}{\partial T}\ ;\quad p = -\frac{\partial\Omega}{\partial V}$$

$$\langle E\rangle = \mu\langle N\rangle - \frac{\partial}{\partial\beta}\ln Q$$

$$\Omega = -pV$$

Thus, $pV = -\Omega = kT\ln Q$ {short cut to equation of state

- Completely General!

i.e. System can be interacting, non-interacting, quantum or classical.

This is the Grand Canonical Ensemble approach.

Refs: Mandl Sec. 11.1, 11.7
Bowley & Sanchez Sec. 9.1, 9.2, 9.7, 9.9

Roadmap: To move forward...

- Non-interacting fermions/bosons
- Occupation number representation $\{n_r\}$

$$E(\{n_r\}) = \sum_r \varepsilon_r n_r \,, \quad N = \sum_r n_r$$

$$Q_{\text{Fermion}} = \sum_{N=0}^{\infty} \sum_{\substack{\text{all } \{n_j\} \\ \text{such that } \sum_j n_j = N \\ \text{AND } n_j = 0, 1 \text{ for all } j}} e^{-\beta \sum_j (\varepsilon_j - \mu) n_j} = \underset{\substack{\uparrow \\ \text{product} \\ \text{over single-particle states}}}{\prod_r} \left(1 + e^{-\beta(\varepsilon_r - \mu)}\right)$$

$$Q_{\text{Boson}} = \sum_{N=0}^{\infty} \sum_{\substack{\text{all } \{n_j\} \\ \text{such that } \sum_j n_j = N \\ \text{AND } n_j = 0, 1, 2, \ldots \text{ for all } j}} e^{-\beta \sum_j (\varepsilon_j - \mu) n_j} = \underset{\substack{\uparrow \\ \text{product} \\ \text{over single-particle states}}}{\prod_r} \frac{1}{1 - e^{-\beta(\varepsilon_r - \mu)}}$$

(see next chapter)