

0.1 Review

What should we learn?

- Structure of the subject, systems, physical phenomena, basic concepts, fundamental methods, principles, assumptions, laws, theorems, conclusions, applications, typical problems
- Important methods, calculations and examples
- Advanced topics

What should we emphasize?

- Features of the subject $\left\{ \begin{array}{l} \text{many particles} \\ \text{thermal phenomena} \\ \text{stochastic process} \end{array} \right.$
- Difference from other subjects
do not solve equations of motion
statistical methods

0.1.1 Thermodynamics

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Systems: macroscopic systems

Problems: heat, heat conduction, engine, thermodynamic processes

Basic concepts: temperature, other parameters P, V, W ,
heat capacity, internal energy
entropy, other thermodynamic potentials F, H, G

Fundamental methods: logical deduction, calculus

Principles:

- For a system, the number of independent parameters is fixed
- Everything is possible if it is not contradicting the laws

laws:

- the zeroth law
thermal equilibrium \rightarrow temperature \rightarrow equations of state
- The first law
heat is energy \rightarrow energy conservation
- The second law

$$\int_A^B \frac{dQ}{T} \leq S_B - S_A$$

"=" is for a reversible process

the key point:

T, U, S are functions of state but Q, W are not

Typical problems:

- How to calculate some observables
- How to express unmeasurable quantities with measurable quantities.

A general method: characteristic thermodynamic potentials:

$$U(S, V) \quad A(T, V)$$

Important example: The ideal gas!

Difficult but important

- logical argument for the second law
- derivation of the entropy

0.1.2 Statistical mechanics

Systems: macroscopic systems composed of a large number of elements

Purpose:

- Derive thermodynamics

- Calculate physical observables

Fundamental methods: Statistical methods

Basic concepts:

- Ensemble
physically not very important, just a set of microscopic states
- Probability distribution $\rho(p, q)$ of the microscopic states
- Thermodynamic limit

$$V \rightarrow \infty, N \rightarrow \infty, \frac{N}{V} \rightarrow \text{finite}$$

Assumption: e.g., for an ideal gas the interactions are negligible but the system can reach the equilibrium.

Principle:

- Microscopic time average is equivalent to ensemble average

$$\langle O \rangle = \frac{1}{Z} \int dp dq \rho(p, q) O(p, q)$$

- In thermodynamic limit,

$$\frac{\langle O^2 \rangle - (\langle O \rangle)^2}{(\langle O \rangle)^2} \rightarrow 0$$

this is very important.

- For an isolated system,

$$\rho(p, q) = \begin{cases} \text{const} & E \leq H \leq E + \Delta \\ 0 & \text{otherwise} \end{cases}$$

This is based on ergodicity.

For quantum systems, probably one might assume the system is not really isolated.

Three important ensembles

— the names of the "ensemble" are not very important, but the corresponding macroscopic conditions are very important

- Microcanonical ensemble
isolated: energy E , number of particles are microscopically conserved
no work is done, no heat exchange with environments
- Canonical ensemble
Number of particles is conserved
in contact with a heat reservoir of temperature T
- Grand canonical ensemble
In contact with a heat reservoir
Number of particles is not conserved

Important Theorems

- For a canonical ensemble

$$\rho(p, q) \sim e^{-H(p,q)/kT}$$

- For a grand canonical ensemble

$$\rho(p, q, N) \sim e^{(\mu N - H(p,q))/kT}$$

μ is the chemical potential

$$\mu = \frac{\partial A(N, V, T)}{\partial N}$$

i.e. the free energy (or energy) needed to remove a particle.

How to derive the above results are important but somewhat difficult.
At least, we should know

- The rough ideas how to do it.
- Three ensembles are equivalent in the sense of calculating physical observables in thermodynamic limit.
why? What is the difference?

Applications:

Microcanonical ensemble

It is not very convenient for calculations

$$\langle O(p, q) \rangle = \int_{E < H(p, q) < E + \Delta} \text{const } O(p, q) dp dq$$

even for quasi-independent particles.

Still important

- starting point of statistical mechanics
- some examples

Thermodynamics

The entropy

$$S(E, V) \equiv k \log \Gamma(E)$$
$$\Gamma(E) \equiv \int_{E < H(p, q) < E + \Delta} dp dq$$

— the number of microscopic states with energy E

- extensive
- satisfying the second law

The proof is difficult but important

The key point: if (N, V) is divided into (N_1, V_1) and (N_2, V_2)

$$S(E, V) = S_1(\bar{E}_1, V_1) + S_2(\bar{E}_2, V_2)$$

\bar{E}_1 and \bar{E}_2 are the average energy of the subsystems, dominating in thermodynamic limit.

The temperature is defined by

$$\frac{1}{T} \equiv \left(\frac{\partial S(E, V)}{\partial E} \right)_V$$

The pressure

$$P \equiv T \left(\frac{\partial S}{\partial V} \right)_E$$

then, from

$$dS(E, V) = \left(\frac{\partial S}{\partial E} \right)_V dE + \left(\frac{\partial S}{\partial V} \right)_E dV$$

we obtain the first law

$$dE = TdS - PdV$$

— This is also the way to remember the definitions of T and P .

From $E(S, V)$ we may obtain the full thermodynamics.

An important example

A system composed of quasi-independent identical particles, e.g., ideal gas.

μ space: the space spanned by the single particle coordinates (p, q)
(what is Γ space?)

Divide the region where particles may appear into K cells

Count the number of particles in the i -th cell, denote it n_i ,

then

$$\sum_i^K n_i = N, \quad \sum_i \epsilon_i n_i = E$$

ϵ_i is the representative energy in the cell

A set of $\{n_i\}$ may correspond to many microscopic states, we denote it $\Omega\{n_i\}$, then

$$\Gamma(E) = \sum_{\{n_i\}} \Omega\{n_i\}$$

$\Omega\{n_i\}$ can be written down

$$\Omega\{n_i\} = \frac{N!}{\prod_i n_i!}$$

hint: interchange of particles inside a cell does not lead to a new state.

However, the sum over $\{n_i\}$ is difficult.

The tricky point here:

In thermodynamic limit, the average $\{\bar{n}_i\}$ dominates the sum.

Methods:

- $\log n_i! \simeq n_i(\log n_i - 1)$
- Lagrange multiplier
 $\Rightarrow \bar{n}_i = e^{-\alpha - \beta\epsilon_i}$

This is the so-called Boltzmann distribution

Thermodynamics

Define

$$Z(\beta, V) = \sum_i e^{-\beta\epsilon_i}$$

then

$$\begin{aligned} N &= e^{-\alpha} Z(\beta, V) \\ E &= -N \frac{\partial \log Z(\beta, V)}{\partial \beta} \end{aligned}$$

Boltzmann theory is for reading only
Ensemble theory

$$\begin{aligned} S(E, V) &\equiv k \log \Gamma(E) \\ &\simeq k \log \Omega\{\bar{n}_i\} \end{aligned}$$

$\Rightarrow S(E, V)$ is expressed through $Z(\beta, V)$
then

$$\begin{aligned} \frac{1}{T} &\equiv \frac{\partial S}{\partial E} \\ P &\equiv T \left(\frac{\partial S}{\partial V} \right)_E = - \left(\frac{\partial E}{\partial V} \right)_S \end{aligned}$$

Canonical ensemble
The partition function

$$Q_N(V, T) \equiv \int d^{3N} p d^{3N} q e^{-H(p, q)/kT}$$

Thermodynamic is obtained from

$$Q_N(V, T) = e^{-A(V, T)/kT}$$

Further, observable

$$\langle O(p, q) \rangle = \frac{1}{Q_N(V, T)} \int d^{3N} p d^{3N} q e^{-H/kT} O(p, q)$$

Applications

- Equipartition theorem
- Ideal gas
- Quasi-independent particles
from $Q_N(V, T) \rightarrow A(V, T) \rightarrow S \rightarrow$ thermodynamics

- Ising model (somewhat difficult)

Grand canonical ensemble

Γ space: spanned by (p, q, N)

$$\rho(p, q, N) \propto e^{(\mu N - H)/kT}$$

The grand partition function

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

$$\mu = \left(\frac{\partial A(N, V, T)}{\partial N} \right)_{V, T}$$

Equation of state

$$\begin{cases} \frac{PV}{kT} = \log Z(\mu, V, T) \\ \frac{\bar{N}}{kT} = \frac{\partial}{\partial \mu} \log Z(\mu, V, T) \end{cases}$$

$$\text{i.e. } \mu = \mu(\bar{N}, V, T) \quad \Rightarrow \quad P = P(\bar{N}, V, T)$$

Internal energy

Let $y = e^{\beta \mu}$

$$U = - \frac{\partial}{\partial \beta} \log Z(y, V, T) \Big|_{y, V}$$

$$= U(\bar{N}, V, T)$$

if we consider \bar{N} is fixed, it looks like a canonical ensemble

$$S = \int_0^T dT \frac{C_V}{T}$$

$$A = U - TS$$

$$= A(\bar{N}, V, T)$$

$$dA = \frac{\partial A}{\partial V} dV + \frac{\partial A}{\partial T} dT + \frac{\partial A}{\partial \bar{N}} d\bar{N}$$

$$= -PdV - SdT + \mu d\bar{N}$$

$$\Rightarrow dU = d(A + TS)$$

$$= PdV + TdS + \mu d\bar{N}$$

An important example: an ideal gas

$$\begin{aligned}
 Q_N &= \frac{1}{N!} \left(\frac{V}{\lambda^3} \right)^N & \lambda &= \left(\frac{1}{2\pi m k T} \right)^{1/2} \\
 Z(\mu, V, T) &= \sum_{N=0}^{\infty} e^{\beta \mu N} \left(\frac{V}{\lambda^3} \right)^N \frac{1}{N!} \\
 &= \exp \left(\frac{e^{\beta \mu} V}{\lambda^3} \right) \\
 \frac{\bar{N}}{kT} &= \frac{\partial}{\partial \mu} \log Z(\mu, V, T) = \frac{V}{\lambda^3} \beta e^{\beta \mu} \\
 \therefore \bar{N} &= \frac{V}{\lambda^3} e^{\beta \mu}, & \beta \mu &= \log \frac{\bar{N} \lambda^3}{V} \\
 \frac{PV}{kT} &= \log Z(\mu, V, T) = \bar{N}
 \end{aligned}$$

$$\begin{aligned}
 U(\mu, V, T) &= \frac{\partial}{\partial \beta} \log Z(y, V, T) \\
 &= \frac{\partial}{\partial \beta} \left(\frac{yV}{\lambda^3} \right) \\
 &= \bar{N} \cdot \frac{3}{\lambda} \frac{\partial \lambda}{\partial \beta} \\
 &= \frac{3}{2} \bar{N} k T
 \end{aligned}$$

0.1.3 Quantum statistical mechanics

$$H \phi_n = E_n \phi_n$$

Microcanonical ensemble

$$\overline{\langle O(x) \rangle} = \sum_{n,m} \overline{C_n^*(t) C_m(t)} \langle \phi_n | O(x) | \phi_m \rangle$$

Postulates:

- $\overline{C_n^*(t) C_m(t)} = 0 \quad n \neq m$
- $\overline{C_n^*(t) C_n(t)} = \begin{cases} \text{const} & E < E_n < E + \Delta \\ 0 & \text{otherwise} \end{cases}$

Density matrix

$$\begin{aligned}\rho &= \sum_{E < E_n < E + \Delta} |\phi_n\rangle \langle \phi_n| \\ \Gamma(E) &= T_r \rho = \sum_{\text{all } \phi_n} \langle \phi_n | \rho | \phi_n \rangle \\ S(E, V) &= k \log \Gamma(E)\end{aligned}$$

Canonical ensemble

Density matrix

$$\begin{aligned}\rho &= e^{-\beta H} \\ Q_N(V, T) &= T_r \rho = \sum_{\text{all states}} \langle \phi_n | e^{-\beta H} | \phi_n \rangle \\ \langle O \rangle &= \frac{1}{Q_N} T_r(O e^{-\beta H})\end{aligned}$$

Grand canonical ensemble

$$\begin{aligned}\rho &= e^{-\beta(H - \mu N)} \\ Z(\mu, V, T) &= T_r \rho \\ \langle O \rangle &= \frac{1}{Z} T_r(O \rho)\end{aligned}$$

An ideal gas

grand canonical ensemble!

Applications