

Chapter 10: Part C

Systems of interacting particles

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Purpose of the chapter

- Beyond systems with negligible interactions → realistic
- Some examples for realistic cases
 - solids---lattice vibrations and normal modes
 - non-ideal classical gas
 - Ferromagnetism

For (sufficiently) low temperature

- **In the case, the system is only in the near-ground state. Thus it is not necessary to examine all the possible states.**
- **Only need to investigate the states of energy not far away from the ground state .**
- **Need to introduce new variables; the low-lying excited states can be described in term of Hamiltonian with simple modes of motion (collective modes).**

For (sufficiently) low temperature

➤ **To be specific, one attempts to choose new variables so that the Hamiltonian becomes identical to that of an assembly of weakly interacting particles, when be expressed in term of the variables.**

➤ **For example, a solid**, in which particles interact strongly with each other. At low T , the vibration is small, and collective modes of motion are then the possible sound wave propagate through solid.

➤ **When sound wave are quantized, they exhibit particle-like behavior and act like weakly interacting quasi-particle called photon.**

For (sufficiently) low temperature

- **For example, ferromagnet moment. All spins and associated magnetic moments interact strongly with each other and all point in one dimension at $T=0$.**
- **Small deviation from the perfect alignment constitute the low-lying excited states of slightly higher energy. These deviations can propagate through the ferromagnet like wave (spin wave), and when quantized, have particle-like properties called magnons.**
- **Other system such as liquid Helium near $T=0$ can be described in terms of quasi-particles.**

Another limit situation is very high T .

- Since the interaction between particles are relatively small, it can be taken into account by systematic approximation methods like approximate power series expansions.**
- These yield correction term departing from those where interaction between particles were absent.**
- For example, ordinary gas which is sufficiently dilute that its behavior does not differ greatly from ideal gas.**
- Another example, spins at very high T .**

Ordering at low T and disordering at high T .

➤ At limit of low T , the system are almost completely ordered. (solid is almost rigid; spins in ferromagnet are almost perfectly aligned). And the small departure from the perfect order (ground state) can then be discussed easily.

➤ In the other limit of high T , the system can be almost completely disordered. (the motions of particles in a gas are almost uncorrelated; the spins in a magnet are almost point in a random directions). Then the small derivation from perfect randomness can be discussed easily.

Ordering at low T and disordering at high T .

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From ordering at low T to disordering at high T .

- **Ordering takes place at a certain T (T_c);**
 - Gas can become liquid at a sharply defined T_c ;**
 - A assembly of spins becomes suddenly into ferromagnet**

The reason: the cooperative behavior leads to the sudden transition.

Picture: when a few particles become locally ordered, this facilitates the ordering of more particles further away. (like a row of collapsing dominoes)

From ordering at low T to disordering at high T .

➤ For example:

(1) when a few gas molecules condense to form a liquid, this process helps other molecules to condense;

(2) when a few spins becomes oriented in a same direction, they produce a effective magnetic field which induces neighboring spins to become pointed in the direction;

➤ Such cooperative effects come from correlation between particles. Just since the correlations, the system are difficult to be discussed theoretically.

In principle,

- **It is true that the exact partition function Z would describe all these phenomena;**
- **But it is very difficult to calculate Z when correlated motions of particles must be taken into account.**
- **In this chapter, three examples:**
 - **Solid as an example of an almost ordered system at low T ;**
 - **A slightly nonideal gas as an example of an almost random system at high T ;**
 - **Ferromagnet as an example of cooperative ordering**

Solids

10.1 lattice vibrations and normal modes

Consider a solid consisting of N atoms. Denote the position vector of i th atom of mass m_i by \mathbf{r}_i (its coordinates by x_{i1}, x_{i2}, x_{i3}). Denote the equilibrium positions of this atom by \mathbf{r}_{i0} .

Introduce a variable

$$\xi_{i\alpha} \equiv x_{i\alpha} - x_{i\alpha}^{(0)},$$

where $\alpha = 1, 2, \text{ or } 3$

The kinetic energy of vibration of solid is

$$K = \frac{1}{2} \sum_{i=1}^N \sum_{\alpha=1}^3 m_i \dot{x}_{i\alpha}^2 = \frac{1}{2} \sum_{i=1}^N \sum_{\alpha=1}^3 m_i \dot{\xi}_{i\alpha}^2$$

since $\dot{x}_{i\alpha} = \dot{\xi}_{i\alpha}$

Solids

10.1 lattice vibrations and normal modes

The potential energy $V=V(\dots)$ can be expanded in Taylor's series since $\xi_{i\alpha}$ is small ($i, j \leq N, \alpha, \beta = 1, 2, 3$)

$$V = V_0 + \sum_{i\alpha} \left[\frac{\partial V}{\partial x_{i\alpha}} \right]_0 \xi_{i\alpha} + \frac{1}{2} \sum_{i\alpha, j\gamma} \left[\frac{\partial^2 V}{\partial x_{i\alpha} \partial x_{j\gamma}} \right]_0 \xi_{i\alpha} \xi_{j\gamma} + \dots$$

Since V must have a minimum at r_0 , then

$$\left[\frac{\partial V}{\partial x_{i\alpha}} \right]_0 = 0,$$

$$A_{i\alpha, j\gamma} \equiv \left[\frac{\partial^2 V}{\partial x_{i\alpha} \partial x_{j\gamma}} \right]_0$$

Then

$$V = V_0 + \frac{1}{2} \sum_{i\alpha, j\gamma} A_{i\alpha, j\gamma} \xi_{i\alpha} \xi_{j\gamma}$$

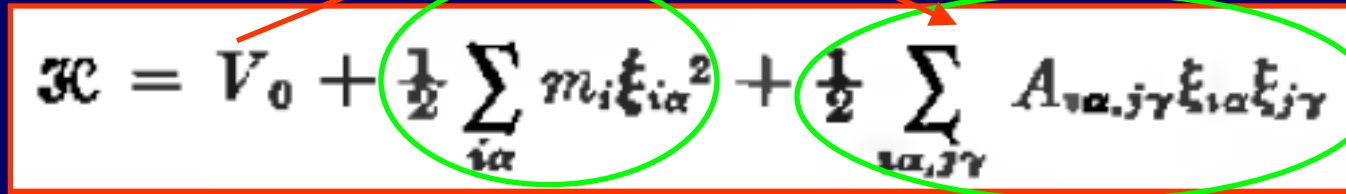
The Hamiltonian

$$\mathcal{H} = V_0 + \frac{1}{2} \sum_{i\alpha} m_i \dot{\xi}_{i\alpha}^2 + \frac{1}{2} \sum_{i\alpha, j\gamma} A_{i\alpha, j\gamma} \xi_{i\alpha} \xi_{j\gamma}$$

Solids

10.1 lattice vibrations and normal modes

The Hamiltonian



The Hamiltonian equation is displayed within a red rectangular box. The equation is $\mathcal{H} = V_0 + \frac{1}{2} \sum_{i\alpha} m_i \dot{\xi}_{i\alpha}^2 + \frac{1}{2} \sum_{i\alpha, j\gamma} A_{i\alpha, j\gamma} \xi_{i\alpha} \xi_{j\gamma}$. A red curved arrow points from the V_0 term to the second summation term. A green oval encircles the first summation term, and another green oval encircles the second summation term.

$$\mathcal{H} = V_0 + \frac{1}{2} \sum_{i\alpha} m_i \dot{\xi}_{i\alpha}^2 + \frac{1}{2} \sum_{i\alpha, j\gamma} A_{i\alpha, j\gamma} \xi_{i\alpha} \xi_{j\gamma}$$

simple complicated

Since involves all possible products of different coordinates.
This reflects that all particles interact with each other and they do not behave like independent particles.

Then how to treat the complicated potential energy?

Solids

10.1 lattice vibrations and normal modes

Then how to treat the complicated potential energy?

Indeed, it can readily be shown that it is possible to go from $3N$ old coordinates $\xi_{i\alpha}$ to some new set of $3N$ generalized coordinates q_r by a linear transformation

$$\xi_{i\alpha} = \sum_{r=1}^{3N} B_{i\alpha,r} q_r$$

A proper choice of coefficients $B_{i\alpha,r}$ transforms H into

$$\mathcal{H} = V_0 + \frac{1}{2} \sum_{r=1}^{3N} (\dot{q}_r^2 + \omega_r^2 q_r^2)$$

q_r is the normal coordinates; ω_r^2 are positive constants

Solids

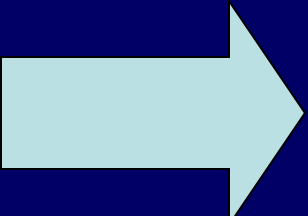
10.1 lattice vibrations and normal modes

For example: 1D atom chain and the coordinate of n-th atom

$$u_n = A_q e^{i(qna - \omega_q t)}$$

Obey equation of motion

$$M \frac{d^2}{dt^2} u_n = -\beta(2u_n - u_{n-1} - u_{n+1})$$


$$\omega_m = 2\sqrt{\frac{\beta}{M}}$$

In 《Solid State Physics》

Solids

10.1 lattice vibrations and normal modes

$$\mathcal{H} = V_0 + \frac{1}{2} \sum_{r=1}^{3N} (\dot{q}_r^2 + \omega_r^2 q_r^2)$$

q_r is the new normal coordinates; ω_r^2 are positive constants. In terms of new variables, H is simply a sum of 3D independent terms each of which refer to a single variable.

For simplicity, consider the 1-D harmonic oscillator H

$$\mathcal{H}_r = \frac{1}{2}(\dot{q}_r^2 + \omega_r^2 q_r^2)$$

The possible quantum state of this oscillator are labeled by quantum number n_r , and $n_r=0, 1, 2, 3, \dots$. The energy is:

$$\epsilon_r = (n_r + \frac{1}{2})\hbar\omega_r$$

Solids

10.1 lattice vibrations and normal modes

The quantum states of the whole system is specified by the set of $3N$ quantum numbers $\{n_1, n_2, n_3, \dots, n_{3N}\}$. n_i can be any integer.

The corresponding energy is the sum of 1D oscillator energies

$$E_{n_1, \dots, n_{3N}} = V_0 + \sum_{r=1}^{3N} (n_r + \frac{1}{2}) \hbar \omega_r$$

Can be written in another form

$$E_{n_1, \dots, n_{3N}} = -N\eta + \sum_{r=1}^{3N} n_r \hbar \omega_r$$

$$-N\eta \equiv V_0 + \frac{1}{2} \sum_r \hbar \omega_r$$

A constant independent of n_r ;
Energy per atom at $T=0$.

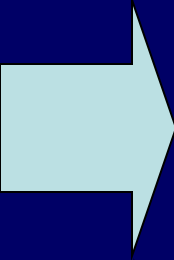
Solids

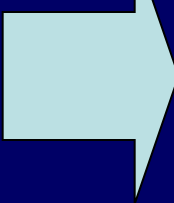
10.1 lattice vibrations and normal modes

Then the calculation of partition function in simple

$$Z = \sum_{n_1, n_2, n_3, \dots} e^{-\beta[-N\eta + n_1\hbar\omega_1 + n_2\hbar\omega_2 + \dots + n_{3N}\hbar\omega_{3N}]}$$

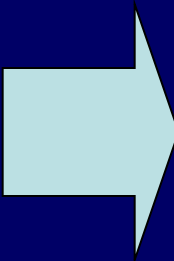
$$= e^{\beta N\eta} \left(\sum_{n_1=0}^{\infty} e^{-\beta\hbar\omega_1 n_1} \right) \cdots \left(\sum_{n_{3N}=0}^{\infty} e^{-\beta\hbar\omega_{3N} n_{3N}} \right)$$


$$Z = e^{\beta N\eta} \left(\frac{1}{1 - e^{-\beta\hbar\omega_1}} \right) \cdots \left(\frac{1}{1 - e^{-\beta\hbar\omega_{3N}}} \right)$$


$$\ln Z = \beta N\eta - \sum_{r=1}^{3N} \ln (1 - e^{-\beta\hbar\omega_r})$$

Solids

10.1 lattice vibrations and normal modes


$$\ln Z = \beta N \eta - \sum_{r=1}^{3N} \ln (1 - e^{-\beta \hbar \omega_r})$$

Introduce the number of normal modes with ω in $[\omega, \omega + d\omega]$

$\sigma(\omega) d\omega \equiv$ the number of normal modes with angular frequency in the range between ω and $\omega + d\omega$.

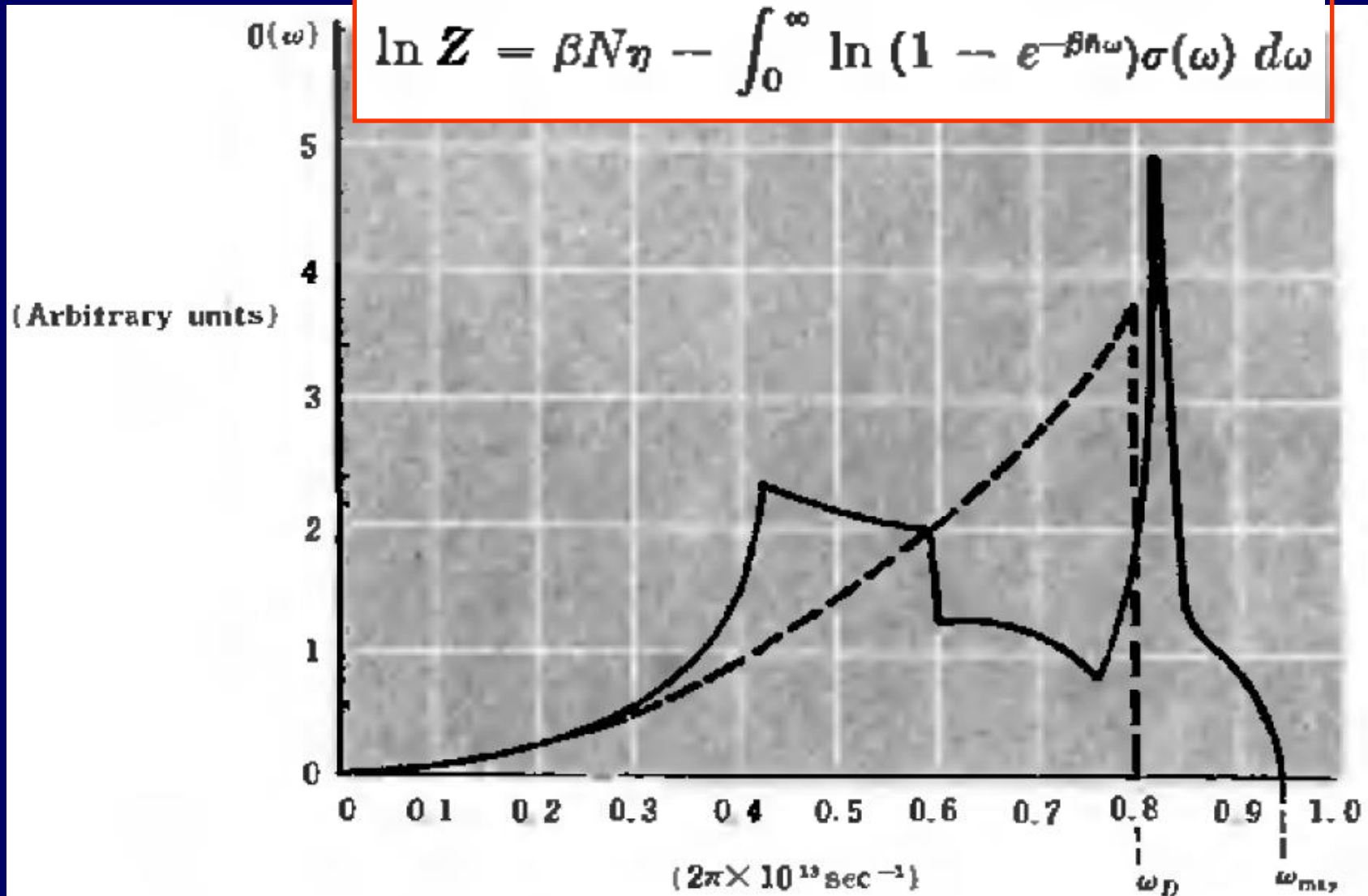
The sum can become the integral

$$\ln Z = \beta N \eta - \int_0^{\infty} \ln (1 - e^{-\beta \hbar \omega}) \sigma(\omega) d\omega$$

Solids

10.1 lattice vibrations and normal modes

$$\ln Z = \beta N \eta - \int_0^\infty \ln(1 - e^{-\beta \hbar \omega}) \sigma(\omega) d\omega$$



Solids

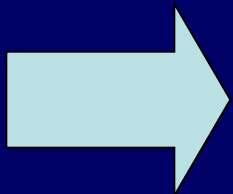
10.1 lattice vibrations and normal modes

The mean energy of the solid becomes

$$\bar{E} = - \frac{\partial \ln Z}{\partial \beta} = -N\eta + \int_0^\infty \frac{\hbar\omega}{e^{\beta\hbar\omega} - 1} \sigma(\omega) d\omega$$

Its heat capacity at constant V

$$C_V = \left(\frac{\partial \bar{E}}{\partial T} \right)_V = -k\beta^2 \left(\frac{\partial \bar{E}}{\partial \beta} \right)_V$$



$$C_V = k \int_0^\infty \frac{e^{\beta\hbar\omega}}{(e^{\beta\hbar\omega} - 1)^2} (\beta\hbar\omega)^2 \sigma(\omega) d\omega$$

Then the rest is to find $\sigma(\omega)$

Solids

10.1 lattice vibrations and normal modes

Let ω_{\max} denotes the maximum frequency, i.e.

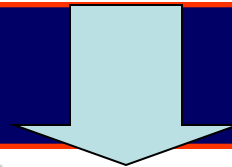
$$\sigma(\omega) = 0 \quad \text{if } \omega > \omega_{\max}$$

If T is high enough $\beta\hbar\omega_{\max} \ll 1$, and $\beta\hbar\omega \ll 1$, then

$$e^{\beta\hbar\omega} = 1 + \beta\hbar\omega + \dots$$

Thus, for high T,

$$C_V = k \int_0^\infty \frac{e^{\beta\hbar\omega}}{(e^{\beta\hbar\omega} - 1)^2} (\beta\hbar\omega)^2 \sigma(\omega) d\omega$$



$$C_V = k \int_0^\infty \sigma(\omega) d\omega = 3Nk$$

$$\int_0^\infty \sigma(\omega) d\omega = 3N$$

Solids

10.2 Debye approximation

The calculation of $\sigma(\omega)$ is complicated.

Two special cases:

a = mean inter-atom separation

λ = wavelength of normal mode of vibration

If $\lambda \gg a$, the normal modes of vibration of elastic medium is very nearly the same to those of actual solid;

If $\lambda \sim a$, the spacing becomes very important, then the actual modes of vibration is quite different from those of elastic continuum.

Means:

$\sigma(\omega)$ is close to $\sigma_c(\omega)$ of continuous medium at low ω ;

$\sigma(\omega)$ differs from $\sigma_c(\omega)$ at high ω .

Solids

10.2 Debye approximation

While there is no limitation on how short a λ or how high ω a continuous medium can have???

Let us examine the normal modes of vibration of the solid considered as an isotropic elastic continuous medium.

$u(r,t)$ denotes the displacement of a point in the medium from its equilibrium position.

In the limit of long wavelength,

$$\xi_{i\alpha}(t) \approx u_{\alpha}(r_i^0, t)$$

$u(r,t)$ must satisfy a wave equation where sound wave propagates in an effective velocity c_s .

Solids

$$\rho_{\kappa} d\kappa = \frac{V}{(2\pi)^3} (4\pi\kappa^2 d\kappa) = \frac{V}{2\pi^2} \kappa^2 d\kappa$$

10.2 Debye approximation

The analysis of normal modes is analogous to Sec 9.9.

$\omega = c_s \kappa$, and the number of possible wave modes with ω in $[\omega, \omega + d\omega]$ is given by

$$\sigma_c(\omega) d\omega = 3 \frac{V}{(2\pi)^3} (4\pi\kappa^2 d\kappa) = 3 \frac{V}{2\pi^2 c_s^3} \omega^2 d\omega$$

3 denotes the 3 directions of polarization of u (one longitudinal one and two transverse ones)

Debye approximates $\sigma(\omega)$ by $\sigma_c(\omega)$ for all the $3N$ low- ω of the elastic continuum. In equation,

$$\sigma_D(\omega) = \begin{cases} \sigma_c(\omega) & \text{for } \omega < \omega_D \\ 0 & \text{for } \omega > \omega_D \end{cases}$$

Solids

$$\rho_k d\kappa = \frac{V}{(2\pi)^3} (4\pi\kappa^2 d\kappa) = \frac{V}{2\pi^2} \kappa^2 d\kappa$$

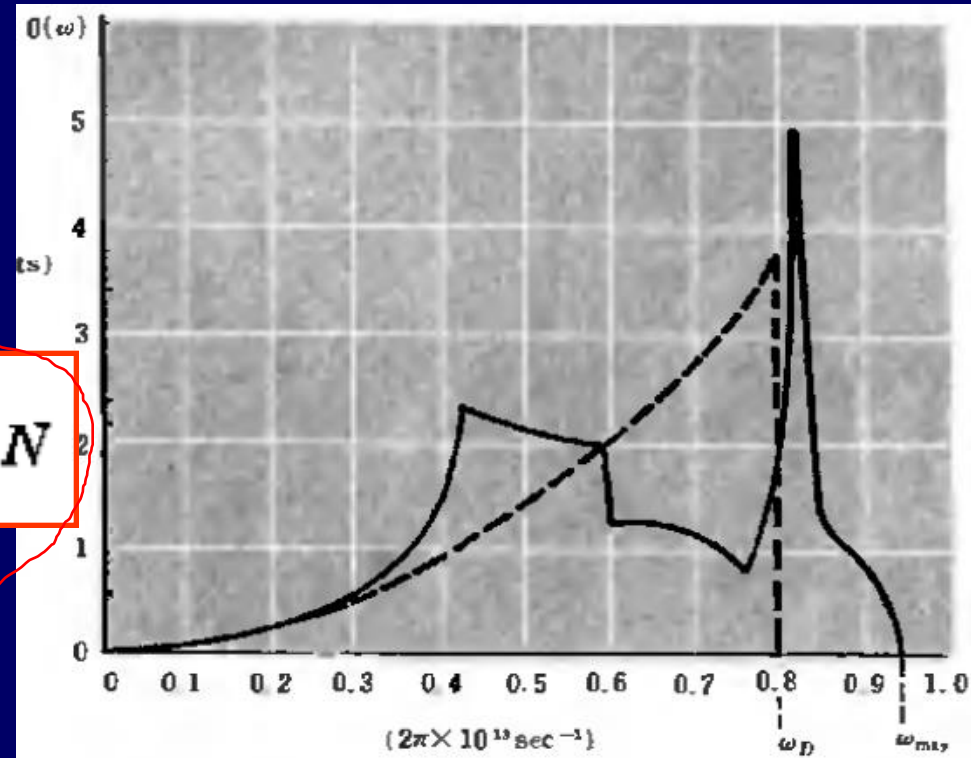
10.2 Debye approximation

ω_D is the Debye frequency and can be given by the total number of $3N$ normal modes

$$\int_0^\infty \sigma_D(\omega) d\omega = \int_0^{\omega_D} \sigma_c(\omega) d\omega = 3N$$

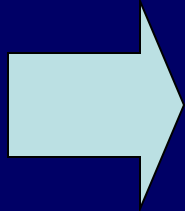
$$\sigma_c(\omega) d\omega = 3 \frac{V}{2\pi^2 c_s^3} \omega^2 d\omega$$

$$\frac{3V}{2\pi^2 c_s^3} \int_0^{\omega_D} \omega^2 d\omega = \frac{V}{2\pi^2 c_s^3} \omega_D^3 = 3N$$



Solids

10.2 Debye approximation



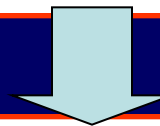
$$\omega_D = c_s \left(6\pi^2 \frac{N}{V} \right)^{1/3}$$

Thus ω_D depends only on sound velocity, and on the number of atom per unit.

Since $c_s \sim 5 \cdot 10^5$ cm/sec and $a \sim 10^{-8}$ cm, $\omega_D \sim 10^{14}$ sec⁻¹.

Using the Debye approximation, the heat capacity becomes

$$C_V = k \int_0^{\omega_D} \frac{e^{\beta\hbar\omega} (\beta\hbar\omega)^2}{(e^{\beta\hbar\omega} - 1)^2} \frac{3V}{2\pi^2 c_s^3} \omega^2 d\omega$$



$$x \equiv \beta\hbar\omega$$

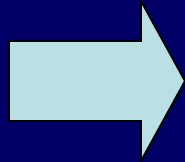
$$C_V = k \frac{3V}{2\pi^2 (c_s \beta \hbar)^3} \int_0^{\beta\hbar\omega_D} \frac{e^x}{(e^x - 1)^2} x^4 dx$$

Solids

$$C_V = k \frac{3V}{2\pi^2 (c_s \beta \hbar)^3} \int_0^{\beta \hbar \omega_D} \frac{e^x}{(e^x - 1)^2} x^4 dx$$

10.2 Debye approximation

$$\omega_D = c_s \left(6\pi^2 \frac{N}{V} \right)^{1/3}$$



$$V = 6\pi^2 N \left(\frac{c_s}{\omega_D} \right)^3$$

Define Debye function

$$f_D(y) \equiv \frac{3}{y^3} \int_0^y \frac{e^x}{(e^x - 1)^2} x^4 dx$$

Then

$$C_V = 3Nk f_D(\beta \hbar \omega_D) = 3Nk f_D \left(\frac{\theta_D}{T} \right)$$

where Debye T is defined

$$k\theta_D \equiv \hbar \omega_D$$

Solids

$$C_V = 3Nk f_D(\beta \hbar \omega_D) = 3Nk f_D\left(\frac{\Theta_D}{T}\right)$$

10.2 Debye approximation

$$f_D(y) \equiv \frac{3}{y^3} \int_0^y \frac{e^x}{(e^x - 1)^2} x^4 dx$$

$T \gg \Theta_D, f_D(\Theta_D/T) \rightarrow 1$. In deed, for small y , one can put $e^x = 1 + x$ in the integrand so that

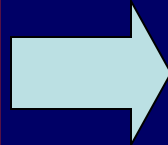
$$f_D(y) \rightarrow \frac{3}{y^3} \int_0^y x^2 dx = 1$$

Then

$$C_V = 3Nk$$

The classic results at high T

$$E = \sum_{i=1}^{3N_a} \left(\frac{p_i^2}{2m} + \frac{1}{2} \kappa_i q_i^2 \right)$$



$$\begin{aligned} \bar{E} &= 3N_a \left[\left(\frac{1}{2} kT \right) \times 2 \right] \\ \bar{E} &= 3N_a kT = 3RT \end{aligned}$$

Solids

$$C_V = k \frac{3V}{2\pi^2 (c_E \beta \hbar)^3} \int_0^{\beta \hbar \omega_D} \frac{e^x}{(e^x - 1)^2} x^4 dx$$

10.2 Debye approximation

At very low T, for relatively
Low ω where $\omega < \omega_D$.

$$f_D(y) \equiv \frac{3}{y^3} \int_0^y \frac{e^x}{(e^x - 1)^2} x^4 dx$$

In the low T limit, the upper limit $\beta \hbar \omega_D = \Theta_D / T$ can be replaced by ∞ , and the integral becomes a constant. Thus for $T < \Theta_D$,

$$C_V \propto \beta^{-3} \propto T^3$$

The result can be more quantitative

$$\int_0^{\infty} \frac{e^x}{(e^x - 1)^2} x^4 dx = 4 \int_0^{\infty} \frac{x^3}{e^x - 1} dx = \frac{4\pi^4}{15}$$

Solids

10.2 Debye approximation

$$\int_0^{\infty} \frac{e^x}{(e^x - 1)^2} x^4 dx = 4 \int_0^{\infty} \frac{x^3}{e^x - 1} dx = \frac{4\pi^4}{15}$$

$$C_V = k \frac{3V}{2\pi^2 (c_s \beta \hbar)^3} \int_0^{\beta \hbar \omega_D} \frac{e^x}{(e^x - 1)^2} x^4 dx$$

$$C_V = \frac{2\pi^2}{5} V k \left(\frac{kT}{c_s \hbar} \right)^3$$

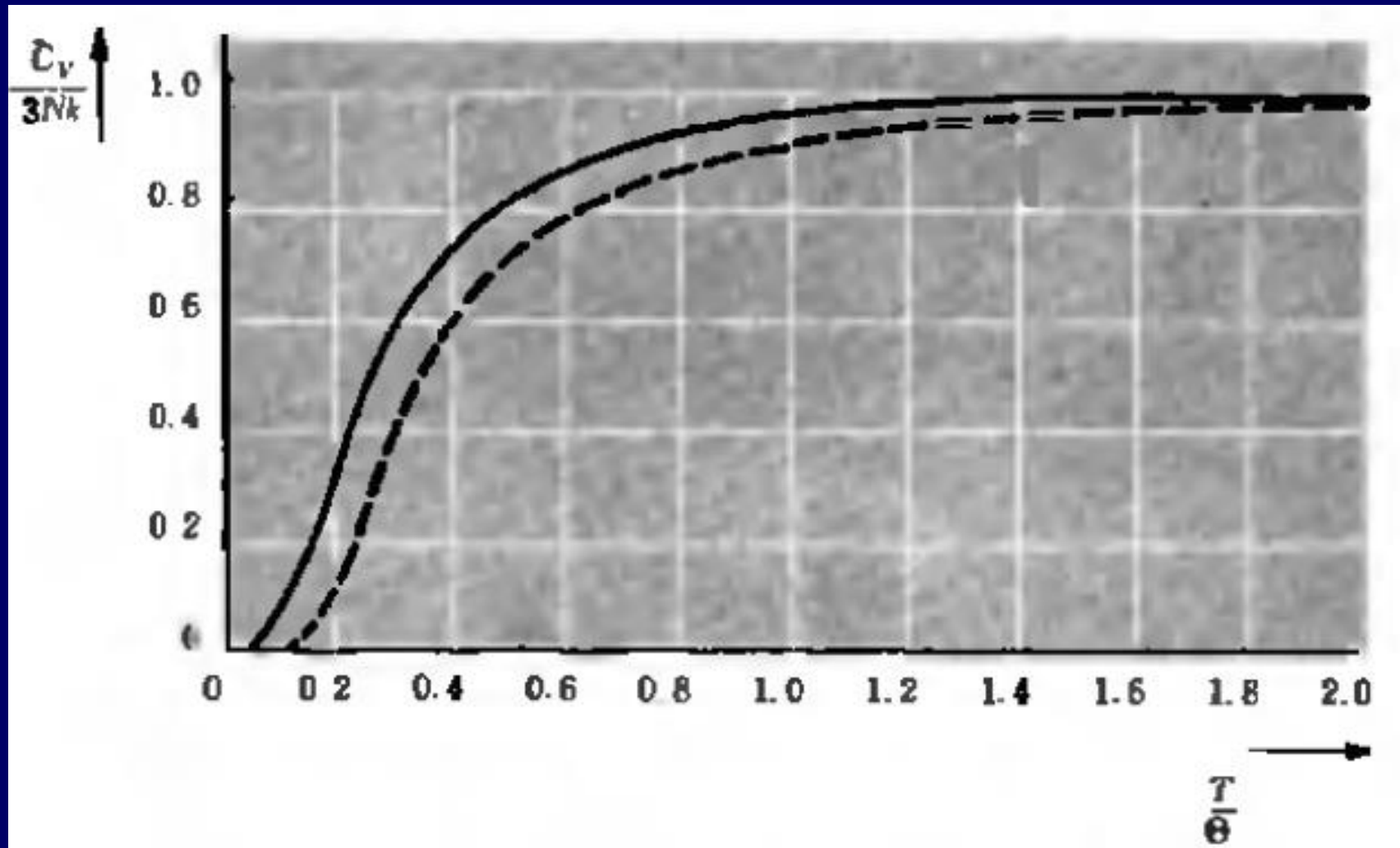
$$C_V = \frac{12\pi^4}{5} N k \left(\frac{T}{\Theta_D} \right)^3$$

$$V = 6\pi^2 N \left(\frac{c_s}{\omega_D} \right)^3$$

$$k\Theta_D \equiv \hbar\omega_D$$

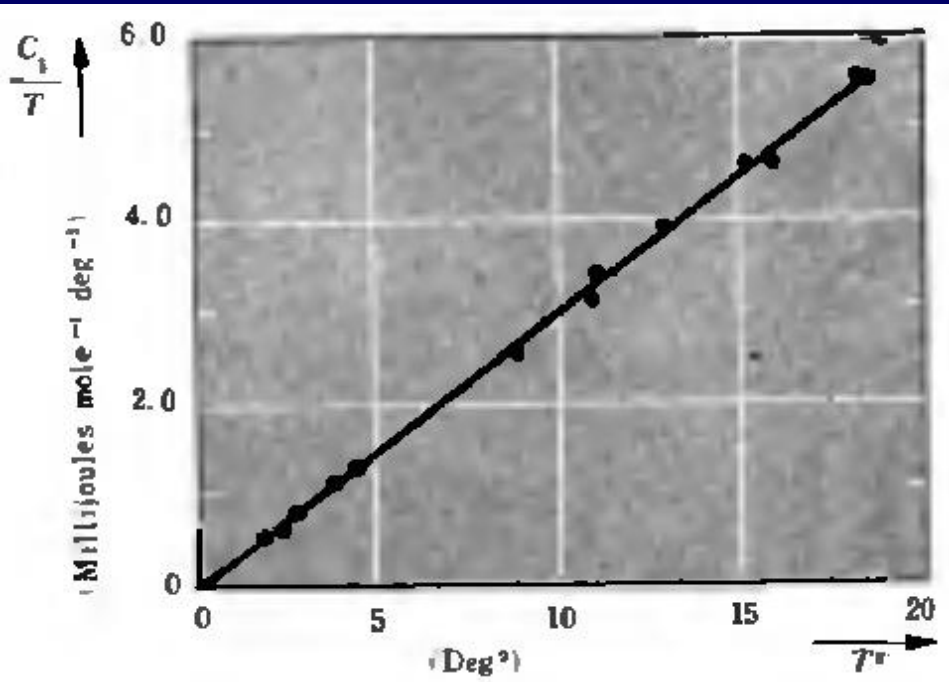
Solids

10.2 Debye approximation

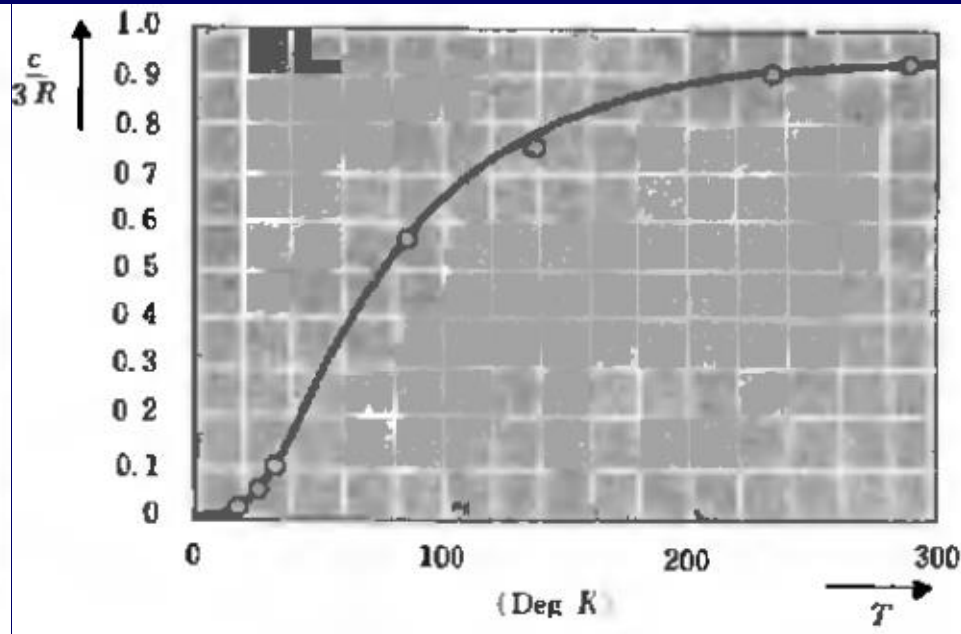


Solids

10.2 Debye approximation



KCl, expt.



Copper: Debye theory & expt.

Solids

10.2 Debye approximation

Table 10 · 2 · 1 Comparison of Debye temperatures obtained from low-temperature specific-heat measurements and calculated from elastic constants*

<i>Solid</i>	Θ_D from specific heat (°K)	Θ_D from elastic constants (°K)
NaCl	308	320
KCl	230	246
Ag	225	216
Zn	308	305

* Compilation taken from C. Kittel "Introduction to Solid State Physics," 2d ed., p. 132, John Wiley & Sons, Inc., New York, 1956.

Nonideal classical gas

10.3 Calculation of partition function for low density

Consider a mono-atomic gas of N identical particles of mass m in a container of V at T .

Assuming T is sufficiently high and $n=N/V$ is sufficiently low. The energy

$$\mathcal{E} = K + U$$

Kinetic energy

$$K = \frac{1}{2m} \sum_{j=1}^N \mathbf{p}_j^2$$

Potential energy

$$U = u_{12} + u_{13} + u_{14} + \dots + u_{23} + u_{24} + \dots + u_{N-1,N}$$

Nonideal classical gas

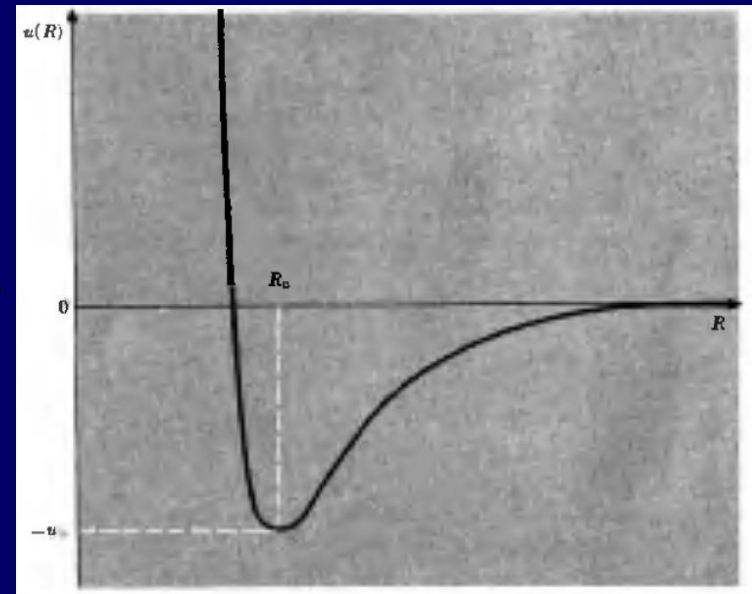
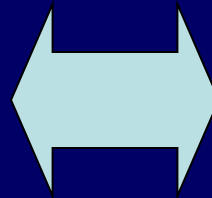
10.3 Calculation of partition function for low density



$$U = \sum_{j=1}^N \sum_{\substack{k=1 \\ j < k}}^N u_{jk} = \frac{1}{2} \sum_{j=1}^N \sum_{\substack{k=1 \\ j \neq k}}^N u_{jk}$$

For simple molecules, it is possible to obtain $U(R)$ by quantum mechanical calculations. A useful semi-empirical potential called Lennard-Jones potential

$$u(R) = u_0 \left[\left(\frac{R_0}{R} \right)^{12} - 2 \left(\frac{R_0}{R} \right)^6 \right]$$



Nonideal classical gas

10.3 Calculation of partition function for low density

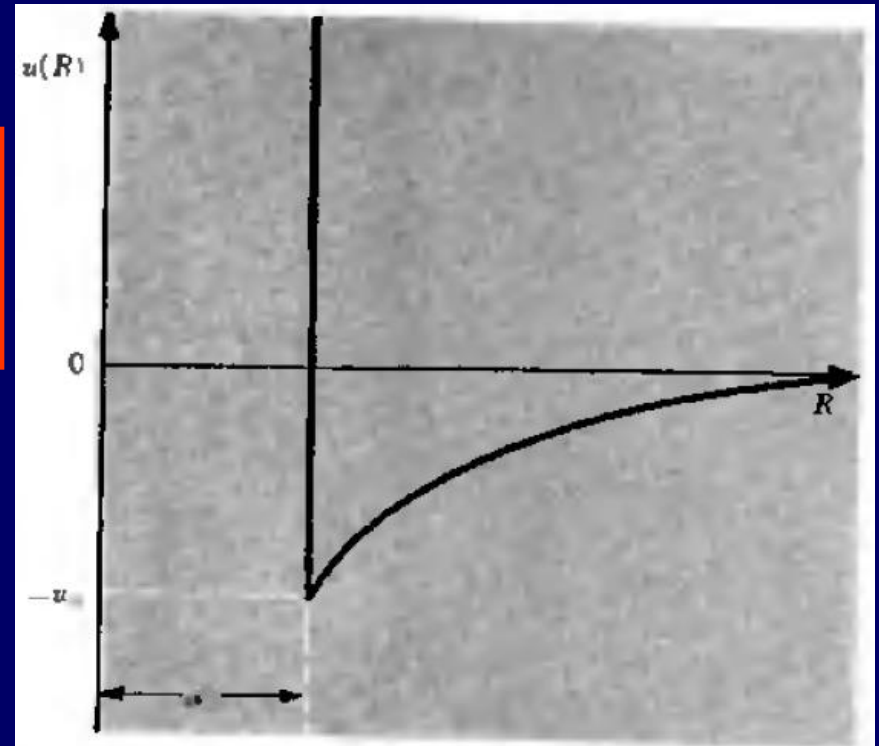
A different potential is a less realistic approx., while is mathematically simple,

$$u(R) = \begin{cases} \infty & \text{for } R < R_0 \\ -u_0 \left(\frac{R_0}{R}\right)^s & \text{for } R > R_0 \end{cases}$$

$s=6$ generally.

$R \rightarrow \infty, U \sim R^{-6}$

$R < R_0, U \rightarrow \infty$



Nonideal classical gas

10.3 Calculation of partition function for low density

To discuss the equilibrium properties, it is necessary to calculate the classic partition function

$$\begin{aligned} Z &= \frac{1}{N!} \iint \cdots \int e^{-\beta(K+U)} \frac{d^3\mathbf{p}_1 \cdots d^3\mathbf{p}_N d^3\mathbf{r}_1 \cdots d^3\mathbf{r}_N}{h^{3N}} \\ &= \frac{1}{h^{3N} N!} \int \cdots \int e^{-\beta K(\mathbf{p}_1, \dots, \mathbf{p}_N)} d^3\mathbf{p}_1 \cdots d^3\mathbf{p}_N \\ &\quad \int \cdots \int e^{-\beta U(\mathbf{r}_1, \dots, \mathbf{r}_N)} d^3\mathbf{r}_1 \cdots d^3\mathbf{r}_N \end{aligned}$$

Denote

$$Z_U \equiv \int \cdots \int e^{-\beta U(\mathbf{r}_1, \dots, \mathbf{r}_N)} d^3\mathbf{r}_1 \cdots d^3\mathbf{r}_N$$



$$Z = \frac{1}{N!} \left(\frac{2\pi m}{h^2 \beta} \right)^{3N} Z_U$$

Nonideal classical gas

10.3 Calculation of partition function for low density

On Z_U

- * is difficult to evaluate for non-ideal gas
- * becomes simple for high T, or $U \rightarrow 0$

$$e^{-\beta U} \rightarrow 1 \quad \longrightarrow \quad Z_U \rightarrow V^N$$

If gas density is not large, it is possible to evaluate Z_U with certain approximation. The mean potential energy

$$\bar{U} = \frac{\int e^{-\beta U} U d^3\mathbf{r}_1 \cdots d^3\mathbf{r}_N}{\int e^{-\beta U} d^3\mathbf{r}_1 \cdots d^3\mathbf{r}_N} = - \frac{\partial}{\partial \beta} \ln Z_U$$

$$Z_U(0) = V^N \text{ for } \beta = 0$$

Integration

$$\ln Z_U(\beta) = N \ln V - \int_0^\beta \bar{U}(\beta') d\beta'$$

Nonideal classical gas

10.3 Calculation of partition function for low density

On Z_U

The mean potential energy

$$\bar{U} = \frac{1}{2}N(N-1)\bar{u} \approx \frac{1}{2}N^2\bar{u}$$

Assume that a particle pair is uncorrelated with other pairs. The probability of a molecule at \mathbf{R}

$$e^{-\beta u(\mathbf{R})} d^3\mathbf{R}$$

Then the mean potential energy

$$\bar{u} = \frac{\int e^{-\beta u} u d^3\mathbf{R}}{\int e^{-\beta u} d^3\mathbf{R}} = -\frac{\partial}{\partial \beta} \ln \int e^{-\beta u} d^3\mathbf{R}$$

The integration is over all \mathbf{R}

Nonideal classical gas

$$\bar{u} = \frac{\int e^{-\beta u} u d^3\mathbf{R}}{\int e^{-\beta u} d^3\mathbf{R}} = -\frac{\partial}{\partial \beta} \ln \int e^{-\beta u} d^3\mathbf{R}$$


10.3 Calculation of partition function for low density

Since $u \sim 0$ and $e^{-\beta u} \sim 1$ practically everywhere when R is small, then

$$\int e^{-\beta u} d^3\mathbf{R} = \int [1 + (e^{-\beta u} - 1)] d^3\mathbf{R} = V + I = V \left(1 + \frac{I}{V}\right)$$

where

$$I(\beta) \equiv \int (e^{-\beta u} - 1) d^3\mathbf{R} = \int_0^{\infty} (e^{-\beta u} - 1) 4\pi R^2 dR$$

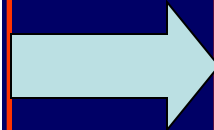

$$\bar{u} = -\frac{\partial}{\partial \beta} \left[\ln V + \ln \left(1 + \frac{I}{V}\right) \right] \approx 0 - \frac{\partial}{\partial \beta} \left(\frac{I}{V} + \dots \right)$$

Nonideal classical gas

$$\bar{u} = \frac{\int e^{-\beta u} u d^3R}{\int e^{-\beta u} d^3R} = - \frac{\partial}{\partial \beta} \ln \int e^{-\beta u} d^3R$$

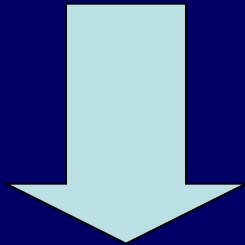
10.3 Calculation of partition function for low density

$$\bar{u} = - \frac{1}{V} \frac{\partial I}{\partial \beta}$$



$$\bar{U} = - \frac{1}{2} \frac{N^2}{V} \frac{\partial I}{\partial \beta}$$

$$\ln Z_V(\beta) = N \ln V - \int_0^\beta \bar{U}(\beta') d\beta'$$



since $I = 0$ for $\beta = 0$,

$$\ln Z_V(\beta) = N \ln V + \frac{1}{2} \frac{N^2}{V} I(\beta)$$

Nonideal classical gas

$$Z = \frac{1}{N!} \left(\frac{2\pi m}{h^2 \beta} \right)^{3N} Z_U$$

10.4 Equation of state and virial coefficients

Equation of state can be easily obtained from Z

$$\bar{p} = \frac{1}{\beta} \frac{\partial \ln Z}{\partial V} = \frac{1}{\beta} \frac{\partial \ln Z_U}{\partial V}$$

since only Z_U involves V .



$$\beta \bar{p} = \frac{\bar{p}}{kT} = \frac{N}{V} - \frac{1}{2} \frac{N^2}{V^2} I$$

Since $n = N/V$, this is of the general form

$$\frac{\bar{p}}{kT} = n + B_2(T)n^2 + B_3(T)n^3 + \dots$$

$B_2, B_3, B_4 \dots$ are the virial coefficients

Nonideal classical gas

$$\beta \bar{p} = \frac{\bar{p}}{kT} = \frac{N}{V} - \frac{1}{2} \frac{N^2}{V^2} I$$

10.4 Equation of state and virial coefficients

Equation of state can be easily obtained from Z since only Z_U involves V .

$$B_2 = -\frac{1}{2}I = -2\pi \int_0^\infty (e^{-\beta u} - 1) R^2 dR$$

A knowledge of u allows an immediate evaluate the correction term to the equation of state

* when R is small, u is large/positive and $(e^{-\beta u} - 1)$ is negative, thus make positive contribution to B_2 ;

* For large R , u is negative and $(e^{-\beta u} - 1)$ is positive, and makes negative contribution to B_2 .

Nonideal classical gas

$$\beta \bar{p} = \frac{\bar{p}}{kT} = \frac{N}{V} - \frac{1}{2} \frac{N^2}{V^2} I$$

10.4 Equation of state and virial coefficients

$$B_2 = -\frac{1}{2}I = -2\pi \int_0^\infty (e^{-\beta u} - 1) R^2 dR$$

A knowledge of u allows an immediate evaluate the correction term to the equation of state

* when R is small, u is large/positive and $(e^{-\beta u} - 1)$ is negative, thus make positive contribution to B_2 ;

* For large R , u is negative and $(e^{-\beta u} - 1)$ is positive, and makes negative contribution to B_2 .

At low T , the negative contribution is dominate;

At high T , it is of minor significance so that B_2 is positive;

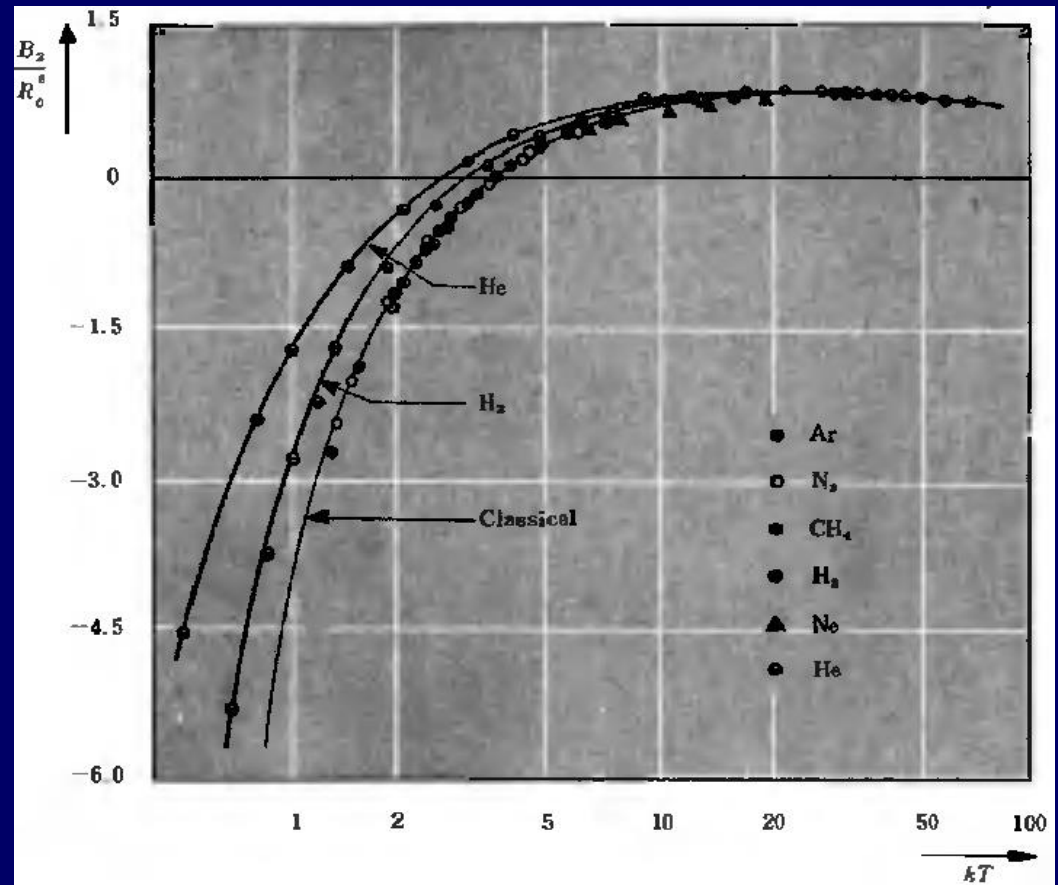
At intermediate T , B_2 must then vanish.

Nonideal classical gas

10.4 Equation of state and virial coefficients

At low T , attractive force is dominant and molecules form the lowest energy state;

At high T , the large kinetic energy overcomes the energy minimum and p increases.



Nonideal classical gas

$$B_2 = -\frac{1}{2}I = -2\pi \int_0^\infty (e^{-\beta u} - 1)R^2 dR$$

10.4 Equation of state and virial coefficients

The van de waals equation

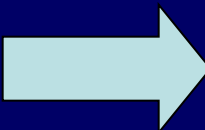
$$B_2 = 2\pi \int_0^{R_0} R^2 dR - 2\pi \int_{R_0}^\infty (e^{-\beta u} - 1)R^2 dR$$


Assume T is high enough that

$$\beta u_0 \ll 1$$

Then

$$e^{-\beta u} \approx 1 - \beta u$$


$$B_2 = \frac{2\pi}{3} R_0^3 - 2\pi\beta u_0 \int_{R_0}^\infty \left(\frac{R_0}{R}\right)^s R^2 dR$$


$$B_2 = \frac{2\pi}{3} R_0^3 \left(1 - \frac{3}{s-3} \frac{u_0}{kT}\right) \quad \text{assuming } s > 3$$

Nonideal classical gas

$$B_2 = -\frac{1}{2}I = -2\pi \int_0^\infty (e^{-\beta u} - 1)R^2 dR$$

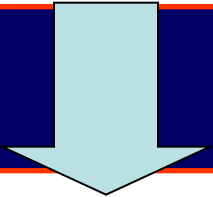
10.4 Equation of state and virial coefficients

The van de waals equation

$$B_2 = \frac{2\pi}{3} R_0^3 \left(1 - \frac{3}{8} \frac{u_0}{kT} \right)$$

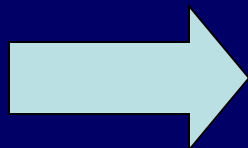
$$b' \equiv \frac{2\pi}{3} R_0^3$$

$$a' \equiv \left(\frac{3}{8} \right) b' u_0$$


$$B_2 = b' - \frac{a'}{kT}$$

Then the equation of state becomes

$$\frac{\bar{p}}{kT} = n + \left(b' - \frac{a'}{kT} \right) n^2$$



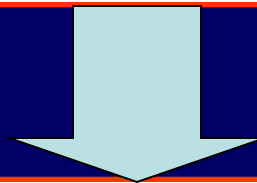
$$\bar{p} = nkT + (b'kT - a')n^2$$

Nonideal classical gas

10.4 Equation of state and virial coefficients

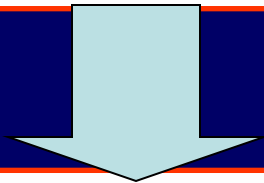
The van de waals equation

$$\bar{p} = nkT + (b'kT - a')n^2$$



$$b'n \ll 1$$

$$\bar{p} + a'n^2 = nkT(1 + b'n) = \frac{nkT}{1 - b'n}$$



$$(\bar{p} + a'n^2) \left(\frac{1}{n} - b' \right) = kT$$

The van de waals equation

Nonideal classical gas

10.4 Equation of state and virial coefficients

The van de waals equation

$$(\bar{p} + a'n^2) \left(\frac{1}{n} - b' \right) = kT$$

$v=V/\nu$, molar volume

$$n = \frac{N}{V} = \frac{\nu N_a}{V} = \frac{N_a}{v}$$

N_a is Avogadro's number and R is gas constant

$$\left(\bar{p} + \frac{a}{v^2} \right) (v - b) = RT$$

with

$$a \equiv N_a^2 a' \quad \text{and} \quad b \equiv N_a b'$$

A and b are related to the parameters describing U

Nonideal classical gas

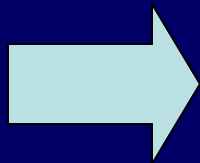
10.5 Alternative derivation of van de Waals eq.

* Focusing a molecule and approximately consider it move in an effective potential $U_e(\mathbf{r})$ due to all other molecules.

* The partition function for the system reduces to a system of N independent particles with U_k and potential energy U_e .

Partition function:

$$Z = \frac{1}{N!} \left[\iiint e^{-\beta(p^2/2m + U_e)} \frac{d^3\mathbf{p} d^3\mathbf{r}}{h^3} \right]^N$$



$$Z = \frac{1}{N!} \left(\frac{2\pi m}{h^2\beta} \right)^{3N} \left[\int e^{-\beta U_e(\mathbf{r})} d^3\mathbf{r} \right]^N$$

Nonideal classical gas

10.5 Alternative derivation of van de Waals eq.

$$Z = \frac{1}{N!} \left(\frac{2\pi m}{h^2 \beta} \right)^{\frac{3}{2}N} \left[\int e^{-\beta U_s(\mathbf{r})} d^3\mathbf{r} \right]^N$$

* Note that there is region that $U_e \rightarrow \infty$, thus the integrand vanishes in these regions of total volume V_x . In the remaining volume $(V - V_x)$, U_e does not vary too rapidly with \mathbf{r} .

* We can replace it by effective constant averaged value \bar{U}_e

$$Z = \frac{1}{N!} \left[\left(\frac{2\pi m}{h^2 \beta} \right)^{\frac{3}{2}} (V - V_x) e^{-\beta \bar{U}_e} \right]^N$$

Nonideal classical gas

10.5 Alternative derivation of van de Waals eq.

There are $N(N-1)/2$ pairs, there exists

$$N\bar{U}_e = \frac{1}{2}N^2\bar{u}$$



$$\bar{U}_e = \frac{1}{2}N\bar{u}$$

Mean inter-molecule energy ($s>3$)

$$\bar{u} = \frac{1}{V} \int_{R_0}^R u(R) 4\pi R^2 dR = - \frac{4\pi u_0}{V} \int_{R_0}^R \left(\frac{R_0}{R}\right)^s R^2 dR$$

Nonideal classical gas

10.5 Alternative derivation of van de Waals eq.

There are $N(N-1)/2$ pairs, there exists

$$\bar{U}_e = \frac{1}{2} N \bar{u} = -a' \frac{N}{V}$$

$$a' \equiv \frac{2\pi}{3} R_0^3 \left(\frac{3}{8} - 3 \right) u_0$$

There are $N(N-1)/2$ pairs, the total excluded volume is

$$\frac{1}{2} N^2 \left(\frac{4}{3} \pi R_0^3 \right)$$

thus

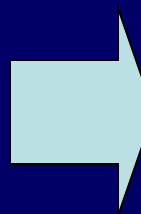
$$V_e = b' N$$

$$b' = \frac{2\pi}{3} R_0^3 = 4 \left[\frac{4\pi}{3} \left(\frac{R_0}{2} \right)^3 \right]$$

Nonideal classical gas

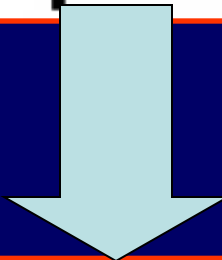
10.5 Alternative derivation of van de Waals eq.

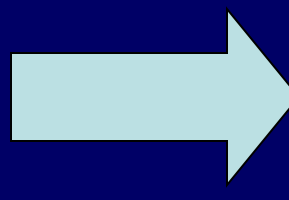
$$Z = \frac{1}{N!} \left[\left(\frac{2\pi m}{h^2 \beta} \right)^{3/2} (V - V_x) e^{-\beta \bar{U}_*} \right]^N$$


$$\bar{p} = \frac{1}{\beta} \frac{\partial \ln Z}{\partial V} = \frac{1}{\beta} \frac{\partial}{\partial V} \left[N \ln (V - V_x) - N\beta \bar{U}_* \right]$$

$$\bar{U}_* = \frac{1}{2} N \bar{u} = -a' \frac{N}{V}$$

$$V_x = b' N$$


$$\bar{p} = \frac{kTN}{V - b'N} - a' \frac{N^2}{V^2}$$


$$\left(\bar{p} + a' \frac{N^2}{V^2} \right) \left(\frac{V}{N} - b' \right) = kT$$

Ferromagnetism

10.6 Interaction between spins

Consider a solid consisting of N identical atoms arranged in a regular lattice. Each atom has a net electronic spin S and associated magnetic momentum

$$\mathbf{\mu} = g\mu_0\mathbf{S}$$

In the presence of external magnetic field H_0 along z direction, the Hamiltonian for atoms interacting with H_0 is

$$\mathcal{H}_0 = -g\mu_0 \sum_{j=1}^N \mathbf{S}_j \cdot \mathbf{H}_0 = -g\mu_0 H_0 \sum_{j=1}^N S_{jz}$$

Ferromagnetism

10.6 Interaction between spins

In addition, each atom also interacts with its neighboring atoms, i.e., exchange interaction. The interaction between atoms j and k is

$$\mathcal{H}_{jk} = -2J \mathbf{S}_j \cdot \mathbf{S}_k$$

J is a parameter describing the strength for exchange interaction.

$$\begin{cases} J > 0 & \text{parallel configuration} \implies \text{ferromagnetism} \\ J < 0 & \text{anti-parallel configuration} \implies \text{antiferromagnetism} \end{cases}$$

Ferromagnetism

10.6 Interaction between spins

Discussions on J

如 $J_{ij} > 0$ 自旋平行时能量最低, 即交换力使自旋平行排列
→ 铁磁态基态 $\uparrow\uparrow\uparrow\uparrow\uparrow$

如 $J_{ij} < 0$ 自旋反平行时能量最低, 即交换力使自旋反平行排列
→ 反铁磁基态 $\uparrow\downarrow\uparrow\downarrow\uparrow\downarrow$

部分 $J_{ij} < 0$ → 可能是亚铁磁性 $\uparrow\downarrow\uparrow\downarrow\uparrow\downarrow$

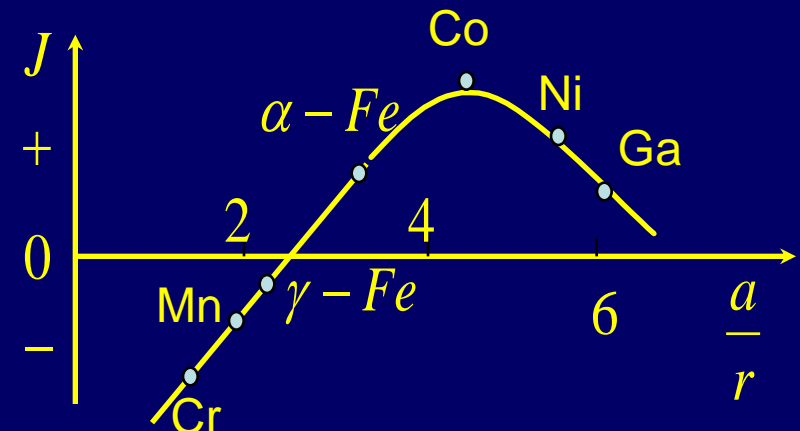
一般实验给出 $d/r > 2.3$ 铁磁性

< 2.3 反铁磁性

式中 d 为原子间距, r 为未满壳层的半径

γ -Fe 是反铁磁体:

- 高温时, $\chi \propto c/(T + \Theta)$
- 很低温时, 在FCC-Cu中微小 γ -Fe 沉淀是反铁磁性的



Ferromagnetism

10.6 Interaction between spins

The exchange interaction is **NOT** interaction between magnetic momentum:

- (1) It is much stronger than the latter;
- (2) It interacts only with neighbor atoms.

In a simple form

$$\mathcal{H}_{jk} = -2J S_{jz} S_{kz}$$

Ising model

The Hamiltonian for all atoms

$$\mathcal{H}' = \frac{1}{2} \left(-2J \sum_{j=1}^N \sum_{k=1}^n S_{jz} S_{kz} \right)$$

Ferromagnetism

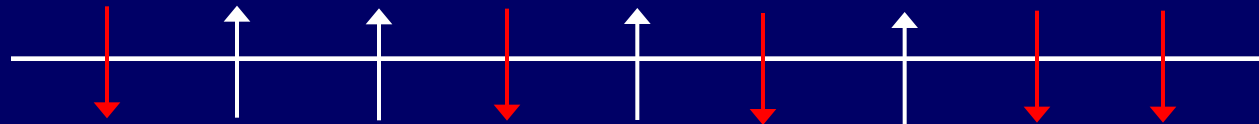
10.6 Interaction between spins

The total Hamiltonian of atoms is

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}'$$

To calculate the thermodynamic functions, such as magnetic momentum, is complicated due to the interactions!

Even $H_0=0$,



Hamiltonian $H = -I \sum \mathbf{s}_i \cdot \mathbf{s}_j$

Partition function $Z = \sum_{\text{all possible configuration}} \exp(-H/k_B T)$

1D: Ising, analytical solution and no ferromagnetic transition

2D: Peierls, exists ferromagnetism transition in high dimension

Kramers, Wannier, primary solution for 2D, FM transition

Osager, strict solution for 2D, FM transition

3D: no strict solution **until now**

Ferromagnetism

10.7 Weiss molecular-field approximation

Focusing attention on a particular atom j , the interactions of atom j is given by

$$\mathcal{H}_j = -g\mu_0 H_0 S_{jz} - 2J S_{jz} \sum_{k=1}^n S_{kz}$$

As an approximation, the sum of the second term can be replaced by a mean field

$$2J \overline{\sum_{k=1}^n S_{kz}} \equiv g\mu_0 H_m$$

H_m : internal field;
molecular field

Then

$$\mathcal{H}_j = -g\mu_0 (H_0 + H_m) S_{jz}$$

effective field

Ferromagnetism

10.7 Weiss molecular-field approximation

With the approximation, it is just the case an atom in an external field $H_0 + H_m$. Then the energy levels are then

$$E_m = -g\mu_0(H_0 + H_m)m_s$$

$$m_s = -S, (-S + 1), \dots, S$$

Similarly to Eq. 7.8.13

$$\overline{S_{jz}} = SB_S(\eta)$$

$$\eta \equiv \beta g\mu_0(H_0 + H_m), \quad \beta \equiv (kT)^{-1}$$

It involves the unknown H_m . Then how to get H_m ?

Ferromagnetism

10.7 Weiss molecular-field approximation

$$\bar{\mu}_z = \frac{\sum_{m=-J}^J e^{\beta g \mu_0 H m} (g \mu_0 m)}{\sum_{m=-J}^J e^{\beta g \mu_0 H m}}$$

$$\bar{\mu}_z = \frac{1}{\beta} \frac{1}{Z_a} \frac{\partial Z_a}{\partial H} = \frac{1}{\beta} \frac{\partial \ln Z_a}{\partial H}$$

$$Z_a = \sum_{m=-J}^J e^{\eta m} = e^{-\eta J} + e^{-\eta(J-1)} + \dots + e^{\eta J}$$

$$Z_a = \frac{e^{-\eta(J+\frac{1}{2})} - e^{\eta(J+\frac{1}{2})}}{e^{-\frac{1}{2}\eta} - e^{\frac{1}{2}\eta}}$$

$$\bar{\mu}_z = g \mu_0 \left[\frac{(J + \frac{1}{2}) \cosh (J + \frac{1}{2})\eta}{\sinh (J + \frac{1}{2})\eta} - \frac{\frac{1}{2} \cosh \frac{1}{2}\eta}{\sinh \frac{1}{2}\eta} \right]$$

$$\bar{\mu}_z = g \mu_0 J B_J(\eta)$$

Ferromagnetism

10.7 Weiss molecular-field approximation

Discussion on H_m .

We cannot distinguish the atom j from any of its neighboring atoms. Then any of the atoms can be equally considered as the j th/central atom. And H_m can be calculated in a self-consistent way

$$\begin{aligned} 2J \sum_{k=1}^n S_{kz} &\equiv g\mu_0 H_m \\ \overline{S_{jz}} &= S B_S(\eta) \end{aligned} \quad \Rightarrow \quad 2J n S B_S(\eta) = g\mu_0 H_m$$

Since

$$\eta \equiv \beta g\mu_0 (H_0 + H_m),$$

Ferromagnetism

10.7 Weiss molecular-field approximation

$$2JnSB_S(\eta) = g\mu_0 H_m$$

$$\eta \equiv \beta g\mu_0 (H_0 + H_m),$$

$$B_S(\eta) = \frac{kT}{2nJS} \left(\eta - \frac{g\mu_0 H_0}{kT} \right)$$

If in the absence of H_0

$$B_S(\eta) = \frac{kT}{2nJS} \eta$$

The solution can be illustrated by drawing the functions in the same figure:

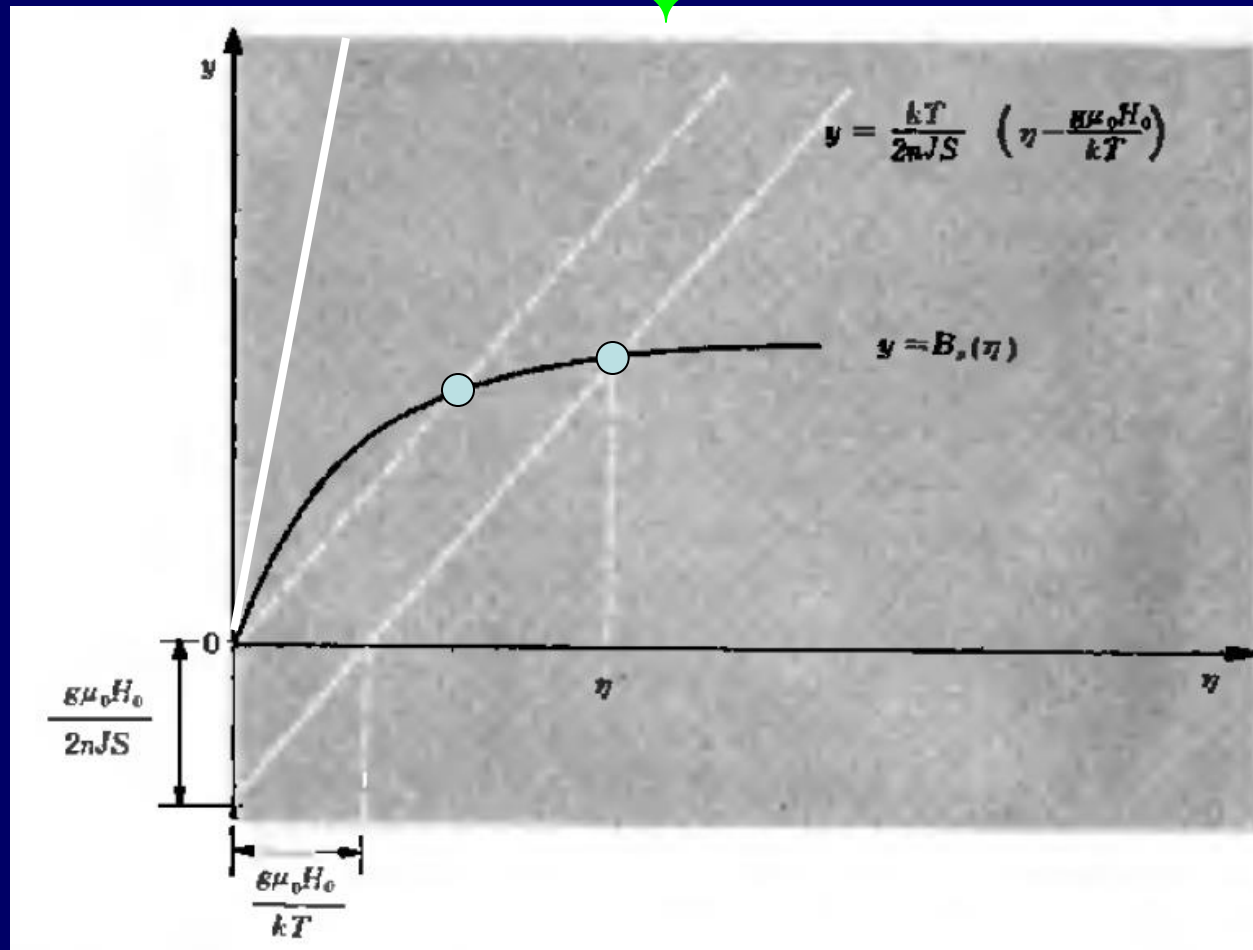
$$y = \frac{kT}{2nJS} \left(\eta - \frac{g\mu_0 H_0}{kT} \right)$$

$$y = B_S(\eta)$$

Ferromagnetism

10.7 Weiss molecular-field approximation

$$y = \frac{kT}{2nJS} \left(\eta - \frac{g\mu_0 H_0}{kT} \right) \quad y = B_s(\eta)$$



Ferromagnetism

10.7 Weiss molecular-field approximation

Once H_m is determined, the total magnetic momentum can be known,

$$\vec{M} = g\mu_0 \sum_j \overline{S_{jz}} = Ng\mu_0 S B_S(\eta)$$

Considering the case of $H_0=0$, if $\eta \neq 0$, it is in ferromagnetic state; if $\eta=0$, paramagnetic state. How can there be solution for $\eta \neq 0$???

The initial slope of $B_S(\eta)$ is larger than that of straight line, then

Ferromagnetism

10.7 Weiss molecular-field approximation

$$\left[\frac{dB_S}{d\eta} \right]_{\eta=0} > \frac{kT}{2nJS}$$

When $\eta \ll 1$, i.e., at high T

$$B_S(\eta) \approx \frac{1}{3}(S+1)\eta$$

Then

$$\frac{1}{3}(S+1) > \frac{kT}{2nJS} \quad T < T_c$$

$$kT_c \equiv \frac{2nJS(S+1)}{3}$$

Curie T

Ferromagnetism

10.7 Weiss molecular-field approximation

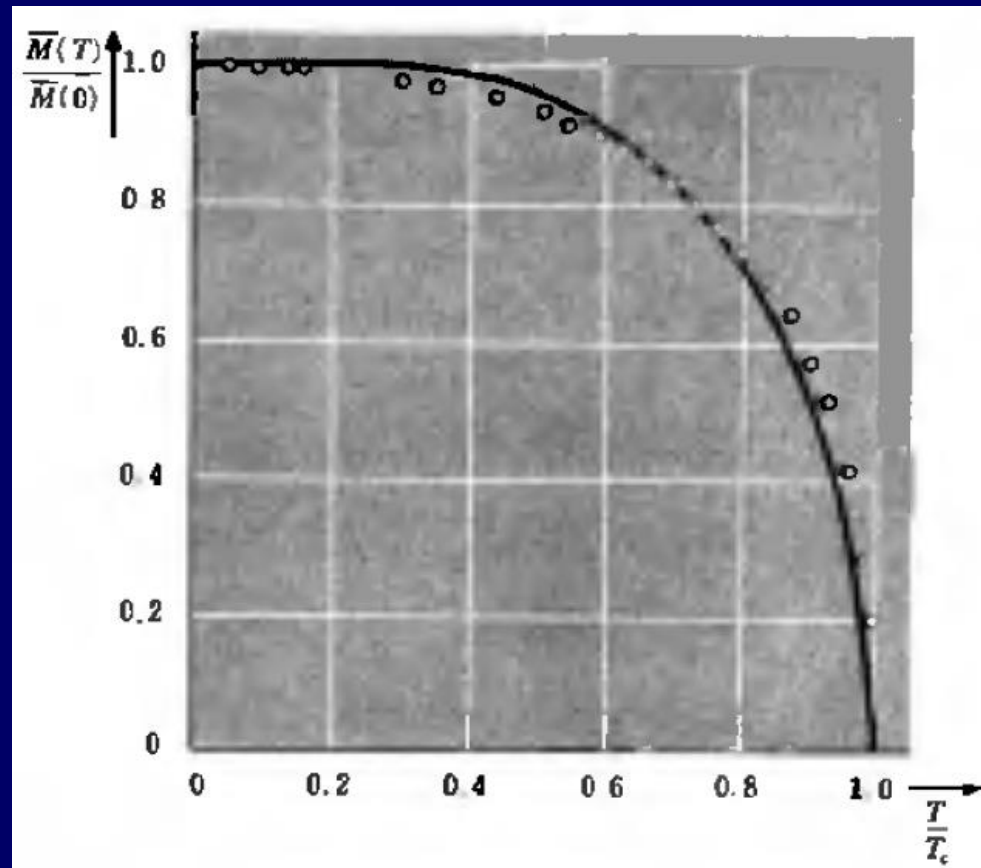
When $T < T_c$

$$y = \frac{kT}{2nJS} \left(\eta - \frac{g\mu_0 H_0}{kT} \right) \quad y = B_J(\eta)$$

can give solution

$T \rightarrow 0, \eta \rightarrow \infty, M \rightarrow Ng\mu_S$

$T \rightarrow T_c, M \rightarrow 0$



Ferromagnetism

10.7 Weiss molecular-field approximation

On magnetic susceptibility in small H_0 and $T > T_c$; η is small, then

$$B_S(\eta) = \frac{kT}{2nJS} \left(\eta - \frac{g\mu_0 H_0}{kT} \right)$$

$$\bar{M} = g\mu_0 \sum_j \bar{S}_{jz} = Ng\mu_0 S B_S(\eta)$$

$$\frac{1}{3} (S + 1) \eta = \frac{kT}{2nJS} \left(\eta - \frac{g\mu_0 H_0}{kT} \right)$$

$$\bar{M} = \frac{1}{3} Ng\mu_0 S(S + 1) \eta$$

$$\eta = \frac{g\mu_0 H_0}{k(T - T_c)}$$

$$\chi = \frac{\bar{M}}{H_0} = \frac{Ng^2\mu_0^2 S(S + 1)}{3k(T - T_c)}$$

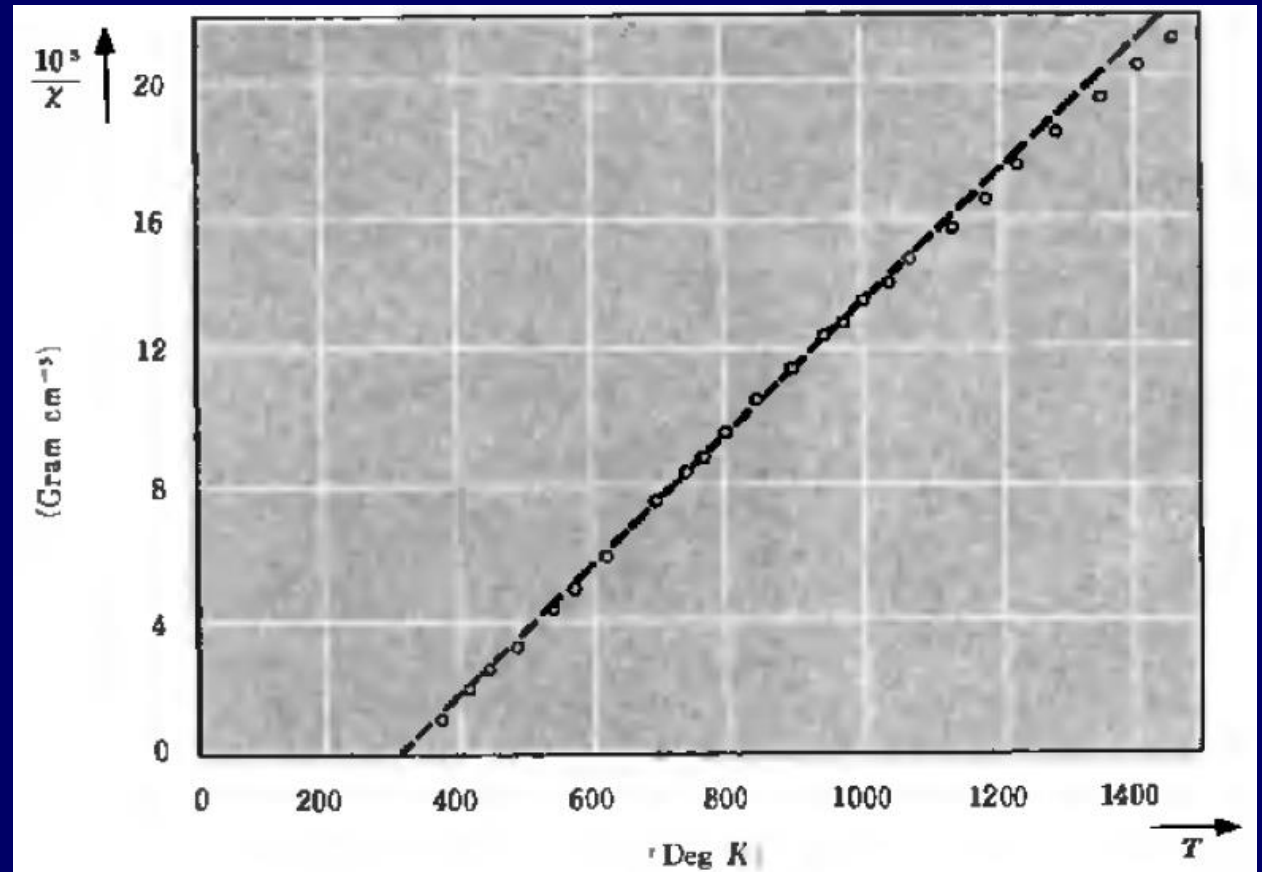
Ferromagnetism

10.7 Weiss molecular-field approximation

$$\chi \equiv \frac{\bar{M}}{H_0} = \frac{Ng^2\mu_0^2 S(S+1)}{3k(T - T_c)}$$

$$\chi = \frac{C}{T - T_c}$$

Curie law



Ferromagnetism

10.7 Weiss molecular-field approximation

Discussion on Weiss mean field theory

- (1) gives almost all the main features of ferromagnetism;
- (2) Not quantitatively correct at $T=T_c$;
- (3) Not quantitatively correct at $T=0$;

Renormalization Group theory for phase transition;
Spin wave theory for $T \sim 0$.

Poisson-Boltzmann (PB) theory

A mean-field theory

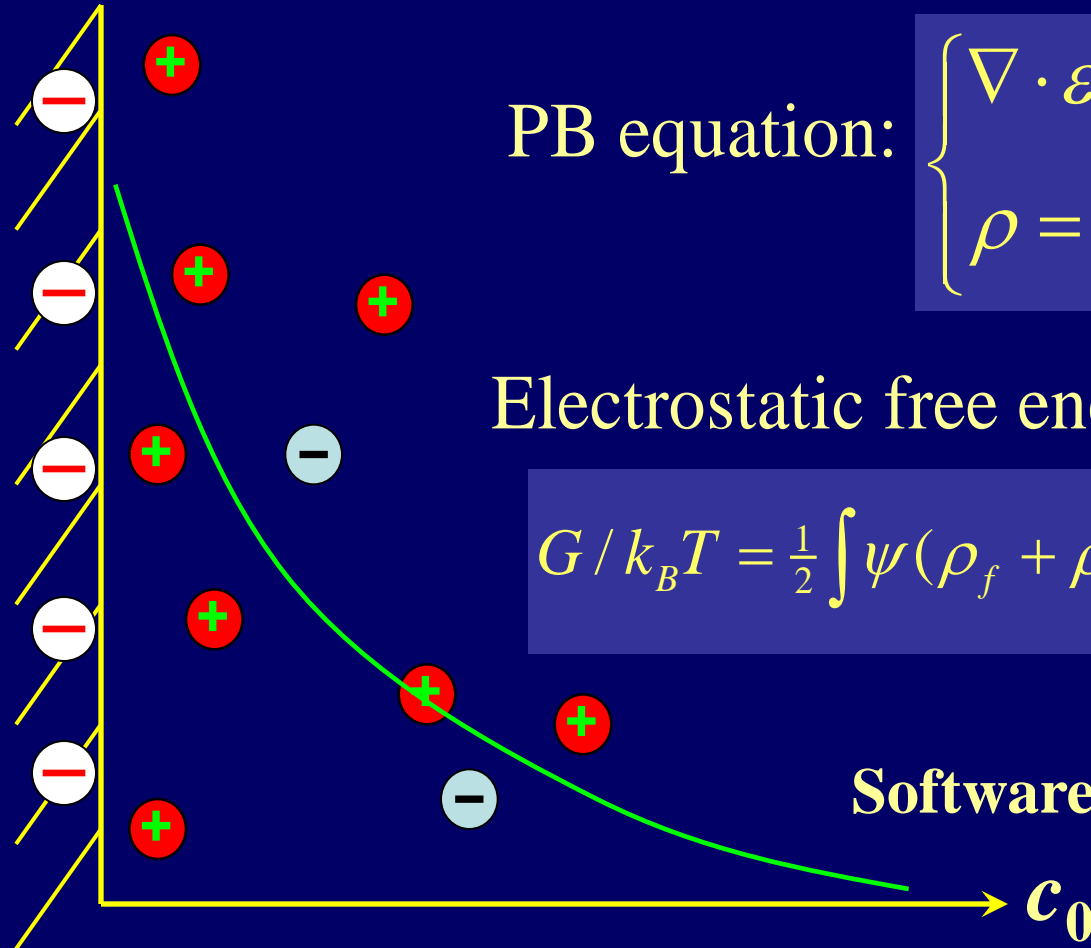
Poisson
equation

PB equation:
$$\begin{cases} \nabla \cdot \epsilon_0 \epsilon \nabla \psi = 4\pi\rho \\ \rho = \left(\rho_f + \sum_{\alpha} z_{\alpha} e c_{\alpha}^0 e^{-z_{\alpha} e \psi / k_B T} \right) \end{cases}$$

Electrostatic free energy:

$$G / k_B T = \frac{1}{2} \int \psi (\rho_f + \rho_m) dv + \int \sum_i \left(c_i \ln \frac{c_i}{c_i^0} - c_i + c_i^0 \right) dv$$

Softwares: DelPhi, UHBD, APBS, etc



Class-work

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Homework (optional)

10.9

Homework

Since $\sigma(\omega) d\omega \propto \kappa^2 d\kappa$ and for spin waves $\omega = A\kappa^2$, it follows that

$$\sigma(\omega) d\omega \propto \omega^{\frac{1}{2}} d\omega$$

Then by (10.1.20)

$$C_V \propto \int_0^\infty \frac{e^{\beta\hbar\omega}}{(e^{\beta\hbar\omega}-1)^2} (\beta\hbar\omega)^2 \omega^{\frac{1}{2}} d\omega$$

Substituting the dimensionless variable $x = \beta\hbar\omega$ we obtain

$$C_V \propto \frac{1}{(\beta\hbar)^{3/2}} \int_0^\infty \frac{e^x}{(e^x-1)^2} x^{5/2} dx$$

The integral is just a constant not involving β . Hence

$$C_V \propto \beta^{-3/2} \propto T^{3/2}$$