Stat Mech. & N.T.

James Peck
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2 Class

NATIONAL

Fall 1947

Made in U. S. A.

THIS BOOK CONTAINS EYE-EASE PAPER

"Easy on the Eyes"

Statistical Mech. and Kinetic Th.

Philip Morrison

Fall 1947

Lecture I. Sept. 26

Text: Mayer & Mayer, Stat. Mech. 1940 Wiley

References:

Gibbs: Ch 1-5, 10, 15

Tolman: Ch 1-4, 9, 11, 13, 14

Fowler: applications & data

Slater: chemical physics

Kennard: K.E. Theory

In order to have a statistical theory, it is necessary that the observer contain a large number of atoms.

The Kinetic Theory evolved from attempts to derive the thermal properties of bodies from their

dynamic properties.

Kinetic theory assumes a stable atomic nucleus. Since the classical laws of energy transfer were known this led to a paradox: why was there no energy lost in the atomic collisions. Q.M. explained this paradox: small energy transfers do not follow classical laws.

In solving statistical problems in Kinetic Theory, we are not at liberty to choose the boundary conditions arbitrarily but must ask "what is the probable state of the system initially?"

Kinetic Theory deals with mechanical models.

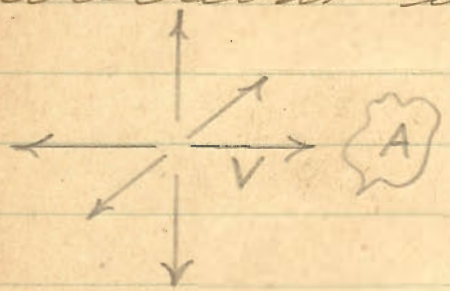
Statistical Mechanics (Gibbs)

deals with general Hamiltonian systems and makes statistical assumptions.

Ideal Gas

$$\text{Pressure} = \frac{\text{F}}{\text{cm}^2} = \frac{d}{dt}\left(\frac{\Sigma mv}{\text{cm}^2}\right)$$

Assume that the molecules move parallel to the Cartesian coordinates and that equal numbers move in the + and - directions along each axis.



The total change in momentum per second at a wall = force

$$= \#\text{mole/cm}^2 \cdot \frac{1}{6} \cdot A \cdot V \cdot 2mV = pA ,$$

$$p = \frac{2}{3}\left(\frac{mV^2}{2}\right)N$$

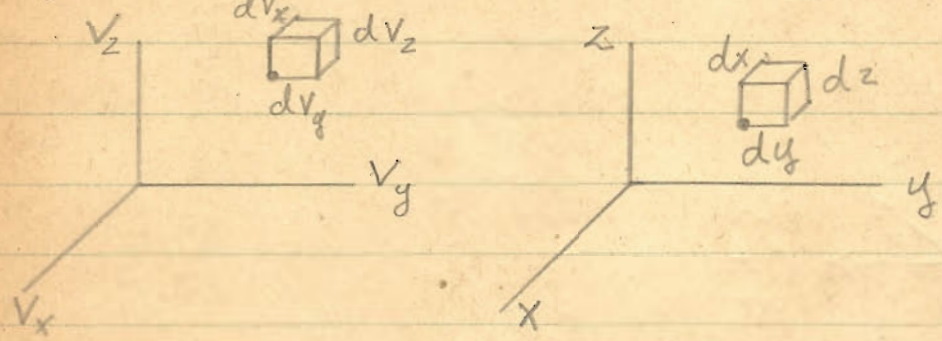
$$pV = \frac{2}{3}(K.E.)_{Total} = \frac{2}{3}T = nRU$$

Temperature, $U \sim T$

General Distribution of Velocities

$f(\bar{V})\,d\bar{V} \equiv$ fraction of mole. having velocities between $\bar{V}$ and $\bar{V} + d\bar{V}$

A molecule is characterized by a point in velocity space and a point in real space.



or a 6 component vector.

$$\bar{P} = (\bar{V}, \bar{r})$$

The state of a gas can be represented by a many component vector.

$$\bar{G} = (\bar{P}_1 \ldots \bar{P}_n)$$

Assume a homogeneous, isotropic gas. $f(\bar{v})$ is spherically symmetric throughout it.

$$f(\bar{v})\,d\bar{v} = f(|\bar{v}|)\,4\pi|\bar{v}|^2\,d|\bar{v}|$$

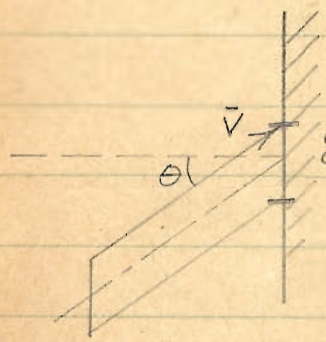
Sept 30

Gas Pressure

$$p\,\delta A = F = \frac{d}{dt}\sum mv$$

Assume a homogeneous isotropic distribution of velocities

$$f(\bar{v})\,d\bar{v} = f(v)\,v^2\,dv\,d\Omega$$



collisions/sec on δA $= N(\delta A\, v\cos\theta)\, f(v)\,v^2\,dv\,d\Omega$

$$p\,\delta A = N(\delta A\, v\cos\theta)(f(v)\,v^2\,dv\,d\Omega)\,2mv\cos\theta$$

$$u \equiv \cos\theta$$

$$\int d\Omega = \int_0^1\int_0^{2\pi} d\phi\,du$$

$$p = 2mN\int_0^1 u^2\,du\int_0^{2\pi}\frac{d\phi}{4\pi}\int v^2 f(v)\,4\pi v^2\,dv$$

$$p = 2mN \cdot \frac{1}{2} \cdot \frac{1}{3} \int v^2 f(v)\, 4\pi v^2 dv$$

V = volume

$$pV = \frac{2}{3} v \cdot L \left[N_0 \int \frac{mv^2}{2} f(v)\, 4\pi v^2 dv \right]$$

$$= \frac{2}{3} v \times \text{mean KE per mole}$$

v = # moles

N_0 = Avogadro number.

$$\frac{2}{3} v \left(\overline{KE}_{\text{molecule}} N_0 \right) = v R T$$

$$\overline{KE}_{\text{molecule}} = \frac{3}{2} \left(\frac{R}{N_0} \right) T = \frac{3}{2} k T$$

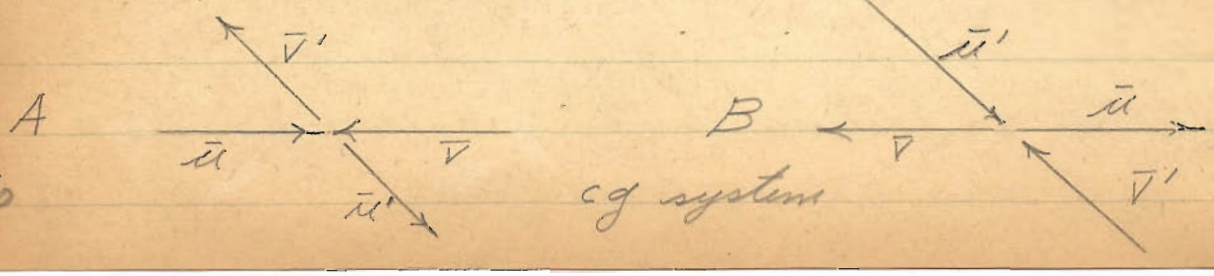
For an ideal gas. Not bad for monatomic noble gases.

Specific Heat per molecule

$$= \frac{d \overline{KE}}{dT} = \frac{3}{2} k$$

Maxwell Boltzman distribution of velocities.

Consider a collision between two identical molecules:



For equilibrium # of molecules going from $u\,v \to u'v'$ = # of molecules going from $u'v' \to uv$

$$c_{uv-u'v'}\, f(u) f(v) = c_{u'v' \to uv}\, f(u') f(v')$$

An examination of figures A and B shows the collision to be identical. Hence $c_{uv-u'v'} = c_{u'v' \to uv}$. This is the assumption of reversibility.

From energy conservation

$$v^2 + u^2 = v'^2 + u'^2$$

Assume a homogeneous isotropic distribution. Take $u' = 0$, u small

$$f(v^2) f(u^2) = f(0) f(u^2 + v^2)$$

$$f(v^2) f(0) + f(v^2) f'(0) u^2 + \ldots$$
$$= f(0) f(v^2) + f(0) f'(v^2) u^2 + \ldots$$

$$\frac{f'(v^2)}{f(v^2)} = \frac{f'(0)}{f(0)} = C$$

$$f(v^2) = a e^{-\alpha v^2}$$

Normalization yields

$$\int_0^\infty a e^{-\alpha v^2} 4\pi v^2 dv = 1$$

$$a = \alpha^{3/2} / 2\pi^{3/2}$$

To get α

$$\tfrac{3}{2} kT = \int \frac{mv^2}{2} f(v) 4\pi v^2 dv$$

$$= \frac{m}{2} \int v^2 \frac{\alpha^{3/2}}{2\pi^{3/2}} e^{-\alpha v^2} 4\pi v^2 dv$$

$$= \frac{2m\alpha^{3/2}}{\sqrt{\pi}} \left(\frac{3}{8} \frac{\sqrt{\pi}}{\alpha^2 \sqrt{\alpha}} \right) = \frac{3}{4} \frac{m}{\alpha}$$

$$\alpha = \frac{m}{2kT}$$

Hence

$$\underline{f(v) 4\pi v^2 dv = \left(\frac{m}{2\pi kT} \right)^{3/2} e^{-\frac{mv^2}{2kT}} 4\pi v^2 dv}$$

Problems:

1. Find $\left(\overline{(E - \bar{E})^2} \right)^{\frac{1}{2}} = \left(\overline{E^2} - \bar{E}^2 \right)^{\frac{1}{2}}$ for a Maxwellian distribution of velocities

2 Show that the # of molecules per sec. leaking thru a small hole is $N A \bar{V}/4$ (Max. dis.) Find mean KE of molecules in leak. How could you determine the temperature of an oven by observations on the leaking molecules.

3. Assume that during the process of evaporation the molecules leaving the surface are in equilibrium with those returning. What mass of Hg can be evaporated per sec at 300° K.

Oct 2.

<u>Streaming</u> For a mass of gas moving by at a uniform velocity $\bar{u}$, the velocity distribution is

$$dn(\bar{V}) = A(\bar{V}-\bar{u})^2 e^{-\frac{m(\bar{V}-\bar{u})^2}{2kT}} d|\bar{V}-\bar{u}|$$

Distribution in a Force Field



$\bar{F} = -mg\,\underline{k}$

$$dn_{z_0} = C\, e^{-\frac{m}{2kT}(v_{x_0}^2 + v_{y_0}^2 + v_{z_0}^2)}\, dv_x\, dv_y\, dv_z$$

A molecule which reaches z from z_0 has velocity given by

$$\frac{m v_{z_0}^2}{2} = \frac{m v_z^2}{2} + mg(z - z_0)$$

$$dn_{z'} = C' e^{-\frac{m}{2kT}(v_x^2 + v_y^2 + v_z^2)}\, dv_x\, dv_y\, dv_z$$

$$= C\, e^{-\frac{m}{2kT}(v_x^2 + v_y^2 + v_z^2) - mg(z - z_0)}\, dv_x\, dv_y\, dv_z$$

Since the number which get to z with velocity v_z = the number which had a velocity, $v_{z_0} = (v_z^2 + 2g(z - z_0))^{1/2}$, at z_0. We require spherical symmetry at all z. Hence:

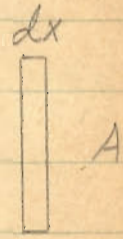
$$dn(v,h) = A e^{-\frac{mv^2}{2kT}} e^{-\frac{mgh}{kT}} v^2 dv$$

$$dn(h) \sim e^{-\frac{mgh}{kT}}$$

Problem: Find the distribution of molecules in a centrifuge

Transport phenomena

Cross section



Prob of a collision in traversing dx = target area / total area.

$$= \frac{\sigma N A dx}{A} = \sigma N \cdot \delta x$$

$\sigma \equiv$ x-section per molecule.

$$dx \sigma N \equiv \frac{dx}{l} \quad \therefore \quad l \equiv \frac{1}{N\sigma} \equiv MF\ path$$

Let $p(x)$ = prob a molecule reaching x has <u>not</u> made a collision

Then

$$p(x+dx) = p(x)\left(1 - \frac{dx}{\ell}\right)$$

$$\frac{dp}{dx} = -p/\ell$$

$$p(x) = e^{-x/\ell}$$

$p(0) = 1$ ok.

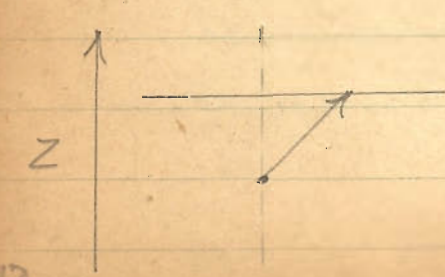
The average distance a molecule goes without a collision is:

$$\bar{x} = \int_0^\infty p(x)\, x\, dx \Big/ \int_0^\infty p(x)\, dx$$

$$= \int_0^\infty x e^{-\frac{x}{\ell}} dx \Big/ \int_0^\infty e^{-\frac{x}{\ell}} dx = \ell$$

For a hard sphere collision $\sigma = \pi(r_1 + r_2)^2$
In other than hard sphere collisions $\sigma = \sigma(\bar{V})$

Transport



$G(z) \equiv$ some property of molecules

$\Gamma(z) \equiv$ flow of $G(z)$/cm²/sec

$$\Gamma(z) = \int d\bar{v}\, n(\bar{v})\, v\, \mu \int G(z-\mu s)\, \frac{e}{\ell}^{-s/\ell}\, ds$$

↑

We assume that the molecules have the G value of their last collision

If G changes only a little in a distance ℓ we can expand

$$= \int d\bar{v} \int \frac{ds}{\ell} e^{-s/\ell} n(\bar{v})\, v\, \mu \left[G(z) - \mu s \frac{dG}{dz} + \dots \right]$$

$$= 0 - \frac{dG}{dz} \int d\bar{v} \int \frac{ds}{\ell} e^{-s/\ell} n(\bar{v})\, \mu v^2 s$$

$$= \frac{1}{3} \frac{dG}{dz} \int \int v\, n(v)\, 4\pi v^2 dv\, e^{-s/\ell} \frac{ds}{\ell}$$

If ℓ independent of v we can integrate to get

$$\Gamma(z) = \frac{1}{3} \bar{s}\, \bar{v} \frac{dG}{dz}$$

Oct 7,

Applications of Transport Equation

1) Heat Conduction = Energy Transfer

$$G(z) = \bar{E}$$

$$\frac{dG}{dz} = \frac{d\bar{E}}{dz} = \frac{d\bar{E}}{dT}\frac{dT}{dz}$$

$$\Gamma(z) \equiv -K\frac{dT}{dz}$$

$$= -\frac{1}{3} n \cdot l \bar{v} \frac{d\bar{E}}{dT}\frac{dT}{dz}$$

$$\frac{d\bar{E}}{dT} = C_{v,\text{molecule}} = \frac{3}{2}k$$

$$\text{Conductivity} = K = \frac{1}{3} n l \bar{v} \left(\frac{C_v}{N_0}\right) = \frac{1}{3}\frac{\bar{v}}{\sigma}\left(\frac{C_v}{N_0}\right)$$

K is independent of density down to values where l becomes too large to permit the expansion in Taylor series. This was striking evidence in support of the K T.

2) Viscosity ≡ Diffusion of transverse momentum



$$G(z) = m u_0 \frac{z}{a}$$

$$\frac{dG}{dz} = m u_0 / a$$

$$\Gamma(z) \equiv -\eta \left(\frac{u_0}{a}\right) = -\eta \frac{d u_0}{dz}$$

$$-\eta \frac{u_0}{a} = -\frac{m u_0}{a} \frac{1}{3} l \bar{v} n$$

$$\eta = \frac{1}{3} m n l \bar{v} = \frac{1}{3} \rho l \bar{v}$$

3) Diffusion ≡ Molecule transfer

$$G(z) = n_1(z) \quad \# \text{ of tagged molecules}$$

$$\frac{dG}{dz} = \frac{dn_1}{dz}$$

$$\Gamma(z) = \# \text{ molecules / cm}^2\text{-sec}$$

$$\Gamma_1 = -\frac{1}{3} l \bar{v} \frac{dn_1}{dz}$$

$$j_z = -D \frac{dn_1}{dz}$$

$$D = \frac{1}{3} l \bar{v}$$

If we have two gases, $\Gamma_1 + \Gamma_2 = 0$, so that the # of molecules per cm^3

is constant.

$$\bar{J} = -D\nabla n_1 = -D\nabla(P c_1)$$

where c_1 = fraction of molecules #1.

Conservation Law

$$\nabla j + \frac{\partial(P c_1)}{\partial t} = Q - S \quad \text{(sources, sinks)}$$

$$j = -D\nabla(P c_1)$$

$$-D\nabla^2(P c_1) + \frac{\partial(P c_1)}{\partial t} = Q - S$$

This is the diffusion equation.

$$D = \frac{l\bar{v}}{3}$$

$$-\frac{l\bar{v}}{3}\nabla^2(P c_1) + \frac{\partial(P c_1)}{\partial t} = Q - S$$

Problem: Solve diffusion eq. for a source in the center of a big room.

A more elaborate transfer theory.

Boltzman eq.

Suppose we compute

$$n(\bar{r}\,\bar{v}\,t)\,d\bar{r}\,d\bar{v}\,dt$$

$$\frac{\partial n}{\partial t} + \bar{v}\cdot\nabla_{\bar{r}} n + \frac{\bar{F}_{ext}}{\rho}\cdot\nabla_{\bar{v}} n$$

$$= \int n(\bar{r}\,\bar{v}')\,n(\bar{r}\,\bar{u}')\,C_{u'v'\to uv}\,du'dv'du$$

$$- \int n(\bar{r}\,\bar{v})\,n(\bar{r}\,\bar{u})\,C_{uv\to u'v'}\,du\,dv'du'$$

Oct 9

Statistical Mechanics

Deals with problem of equilibrium connected with problem of time. No system is in complete equilibrium. Equilibrium is a relative notion. Equilibrium means there are no macroscopic thermodynamic changes over a stated period of time. Or else, according to Mayer and Mayer, equilibrium exists only for stated

reactions.

All dynamic equations are symmetric in time. Hence there is no law in dynamics telling whether time moves backward or forward.
Thermodynamic system and statistical mechanics tell which way time moves.

Problem of probability and knowledge. Each statistical statement is one of probability and of ignorance. The same notion occurs in Q. M. This notion was started by Gibbs.
We make a fundamental distinction between what a system does and what an observer knows about it.

State of a system = detail description of system.

1) Classical

A particle of r degrees of

freedom may be described by $2r$ generalized coordinates, (pq). A system of N molecules by $2Nr$ coordinates. Such a space is phase space, Γ-space. For a single molecule we call it μ-space. A state of a system is specified by one point in phase space.

Let

$$H = \sum_f p_f \dot{q}_f - L(pq\dot{q}t) \quad : p_f = \frac{\partial L}{\partial \dot{q}_f}$$

For any $F(pq)$

$$\dot{F}(pq) = \sum_i \left(\frac{\partial F}{\partial q_i}\frac{\partial H}{\partial p_i} - \frac{\partial H}{\partial q_i}\frac{\partial F}{\partial p_i} \right) = (F\,H)$$

$(F\,H)$ = Poission bracket.

2) Quantum Mechanics

$$\Delta q\, \Delta p \doteq h$$
$$\Delta E\, \Delta t \doteq h$$

In QM we can not give a point.

in phase space because we cannot determine the precise position in phase space.

We can say

$W(q,t)$ = probability of finding a system in a state q at time t = $\psi^*(qt)\psi(qt)$

Instead of phase space we might now use a Hilbert Space, with a non denumerable # of coordinates.

In Q.M., we can only ask for the expectation value of some quantity.

$$\langle F \rangle = \bar{F} = \int d\tau\, \psi^* F \psi = (\psi^* F \psi)$$

$$H\psi + \frac{h}{i}\dot{\psi} = 0$$

Consider special states (eigenstates) where F has definite values F_i

$$F\psi_i = F_i \psi_i$$

Example

$$p\, u_i(q) = p_0\, u_i(q)$$

$$\frac{\hbar}{i}\frac{\partial u}{\partial q} = p_0 u$$

$$u = e^{i p_0 q/\hbar}$$

This tells us the probability of finding q, given p. But $|u|^2 = 1$. Hence we know nothing about q.

Fourier transformation to p-space

$$\psi(p) \sim \int_{-\infty}^{\infty} \psi(q)\, e^{-\frac{i p q}{\hbar}}\, dq$$

This is the Q.M. equivalent of a canonical transformation.

$$\int_{-\infty}^{\infty} e^{\frac{i p q}{\hbar}} e^{-\frac{i p_0 q}{\hbar}}\, dq = \delta(p - p_0)$$

Thus you can take a wave

function with the value of one variable fixed for describing a system.

Most usual example:
Energy operator known precisely
Then one cannot tell the time,
i.e. there is no change in the time behavior.

$$\Psi(qt) = u_E(q)\, e^{iEt/\hbar}$$

$$H u_E = E u_E$$

This is useful. We can find the spectrum of the system i.e. set of values of E for which system can be solved = set of eigenvalues of E.

In general the u_E are orthogonal

$$(E_1 - E_2) \int u_{E_1}^* u_E \, d\tau = 0$$

States are degenerate if they exp to the same E.

If the degeneracy is g-fold, the degenerate state counts g times in the energy spectrum.

$$\Psi(q,t) = \sum_k c_k(t)\, u_k(q)$$

The sum is over all states and becomes an integral in the continuum. $c_k(t)$ = fraction of any state found in any wave function.

Oct 14

Q. M. discription of a system (cont.)
Schroedinger eq.

$$H\Psi = i\hbar \frac{\partial \Psi}{\partial t}$$

$$\Psi = \sum_n c_n(t)\, u_n(q)$$

$$\sum_n c_n(t) H u_n = i\hbar \sum \dot{c}_n(t)\, u_n$$

Multiply by u_m^* and integrate

$$\sum_n c_n(t) \int u_m^* H u_n \, d\tau$$

$$= i\hbar \sum_n \dot{c}_n \int u_m^* u_n \, d\tau$$

$$c_n E_n = i\hbar \dot{c}_n$$

$$c_m = a_m e^{-\frac{iEt}{\hbar}}$$

$$\Psi(qt) = \sum_n a_n e^{-\frac{iE_n t}{\hbar}} u_n(q)$$

$$\bar{E} = \int \Psi^* H \Psi \, d\tau$$

$$= \sum_{mn} \int d\tau \, a_m e^{\frac{iE_m t}{\hbar}} E_n a e^{-\frac{iE_n t}{\hbar}} u_m^* u_n$$

$$= \sum_n a_n^* a_n E_n$$

$|a|^2$ = probability of finding the system in state E_n.

In general, for any operator $F(q)$

$$\bar{F} = \int \Psi^* F \Psi \, d\tau$$

$$= \sum_{nm} \int d\tau \, c_n^* c_m \mu_n^* F \mu_m$$

$$= \sum_{mn} c_n^* c_m F_{nm}$$

where $F_{nm} \equiv \int \mu_n^* F \mu_m \, d\tau$

If F diagonal, $F\mu_n = F_n \mu_n$ and we have the case just treated.

We define the density matrix

$$\rho_{mn} \equiv c_m c_n^* \qquad c\text{'s real}$$

$$\bar{F} = \sum_{mn} F_{mn} \rho_{nm}$$

$$= \sum_m (F\rho)_{mm} = Tr(F\rho)$$

If μ_n = eigenfunction of E_n

$$\rho_{mm} = a_m^* a_n \, e^{-\frac{i}{\hbar}(E_n - E_m)t}$$

The diagonal elements of ρ are real & represent probabilities for which there is a classical analogy. The off diagonal elements are complex and are interpreted as transition probabilities. They have no classical analogy.

Notion of the Ensemble.

Early workers in Q.E. thought they could describe the behavior of a gas by taking a time average over the curve it described in phase-space. (ergotic hypo) This led to difficulty since a curve in space occupies no volume. The next thing that was done was to smear the curve into a tube by admitting

an uncertainty principle (quasi-ergotic hypo). This was ok as long as the initial conditions are chosen correctly. One could not choose, for instance, a gas in a square box in which all the molecules were moving parallel to two walls. So it was found necessary to make statistical assumptions about the initial conditions. Gibbs said why not begin by making a statistical assumption instead of trying to avoid it.

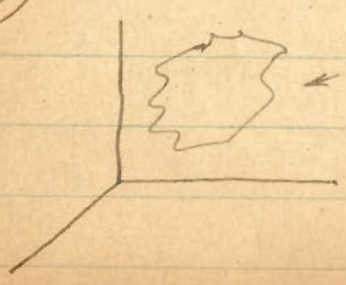
Ensemble defined

A collection of physically identical systems each one of which satisfies all the conditions of know about

the physical system, but which are distributed with respect to variables about which we have no information.

Consider billions of flasks of gas at same T & P, but each having the molecules moving in a different way. If we select a few flasks at random, their average behavior we interpret as representing the average behavior of a gas in a flask. i.e. observed behavior = calc. expected behavior of the ensemble average.

An ensemble is represented by a cloud in phase space



This cloud can change in time, but in doing so paths of the individual elements of the ensemble must not intersect.

The # of elements in a small volume of phase space is given by

$$\delta N = P(p_q) \delta q_1 \dots \delta q_n \delta p_1 \dots \delta p_n$$

where P is a continuous function

Problem: Draw a phase space for a one dimensional S H O. Show path of S H O of energy E. Mark time. Indicate an ensemble for oscillators of energy E, but different initial conditions.

Oct. 16, 1947

The # of points in a volume of phase space

$$dN = \rho(p q t)\, d\tau$$

Normalization $\int_{\text{all space}} \rho\, d\tau = 1$

Ensemble Average

$$\bar{F} = \int \rho F\, d\tau \Big/ \int \rho\, d\tau$$

Liouvilles Theorem



The time rate of change of the # of points in a fixed volume, $d\tau$, in phase space

$$\frac{d}{dt}(\delta N) = \frac{d}{dt}(\rho\, \delta\tau)$$

entering / sec − # leaving / sec

entering thru one "face" $= \rho \dot{q}_1 \, dq_2 \ldots dp_\ldots$

leaving thru one "face"

$$= \left(\rho + \frac{\partial \rho}{\partial q_1} \delta q_1\right)\left(\dot{q}_1 + \frac{\partial \dot{q}_1}{\partial q_1} \delta q_1\right) dq_2 \ldots dp_\ldots$$

Take difference & sum over all "faces"

$$\frac{d}{dt}(\rho \, d\tau) = -d\tau \sum_{i=1}^{f} \left(\dot{q}_i \frac{\partial \rho}{\partial q_i} + \rho \frac{\partial \dot{q}_i}{\partial q_i} + \dot{p}_i \frac{\partial \rho}{\partial p_i} + \rho \frac{\partial \dot{p}_i}{\partial p_i} \right)$$

but $\dot{p} = -\frac{\partial H}{\partial q}$, $\dot{q} = \frac{\partial H}{\partial p}$

If H continuous

$$\frac{\partial \dot{p}}{\partial p} = -\frac{\partial^2 H}{\partial p \partial q} = -\frac{\partial^2 H}{\partial q \partial p} = -\frac{\partial \dot{q}}{\partial q}$$

$$\frac{d\rho}{dt} = -\sum_{i=1}^{f} \left(\frac{\partial \rho}{\partial q_i} \frac{\partial H}{\partial p_i} - \frac{\partial H}{\partial q_i} \frac{\partial \rho}{\partial p_i} \right)$$

$$= -(\rho \cdot H)$$

Since our initial volume was fixed we have

$$\frac{\partial \rho}{\partial t} + (\rho H) = 0$$

or $$\frac{\partial \rho}{\partial t} + \bar{V}_{phase} \cdot \nabla \rho = 0 \quad \text{where } \bar{V} = i\dot{q}_1 + \ldots j\dot{p}_1 + \ldots$$

or $$\frac{D\rho}{Dt} = 0$$

Consider a set of points in phase space

$$\delta N = \rho \, d\tau$$

$$\frac{dN}{dt} = \frac{d\rho}{dt}\delta\tau + \frac{d\,\delta\tau}{dt}\rho = 0$$

$\frac{d\rho}{dt} = 0$ from above theorem. Hence $\delta\tau$ = constant, i.e. The volume occupied by an ensemble in phase space is constant. The points flow like an incompressible fluid.

Problem: Assume cosmic rays have an isotropic distribution far from the earth. Show that close to the earth the distribution is still isotropic within any region in which they can come. (Show for an electric dipole)

The Louville Eq is invariant to a canonical transformation.

A sufficient condition for equilibrium is:

$$\frac{\partial P}{\partial t} = -(PH) = 0$$

∴ The equilibrium P must be a function only of the constants of the motion or its Poisson bracket with H would not be zero.

Grand Assumption: We should try to make the density in phase space as uniform as possible. Desirable because:

1) It will stay that way
2) Invariant to canonical trans.
3) We must assume something.

1) Microcanonical

$$\rho(E) \sim \delta(E - E_0)$$

2) Canonical

$$\rho(E) = Ae^{-E/\theta} = e^{\frac{\psi - E}{\theta}}$$

ψ = a constant θ = a constant = units of E.

$$\int \rho \, d\tau = 1 \quad \therefore \quad e^{-\frac{\psi}{\theta}} = \int e^{-E/\theta} \, d\tau$$

Suppose we bring two systems together and let them interact weakly. We want the distribution in phase space to remain the same.

$$\rho_A = e^{\psi_A - E_A/\theta_A}$$

$$\rho_B = e^{\psi_B - E_B/\theta_B}$$

$$\rho_{A+B} = \rho_A \cdot \rho_B = e^{\frac{\psi_A - E_A}{\theta_A} + \frac{\psi_B - E_B}{\theta_B} - \frac{E_{AB}}{\theta_B} - \frac{E_{AB}}{\theta_A}}$$

For $E_{AB} \ll E_A$

$E_{A+B} \sim E_A + E_B$

$$\rho_{A+B} = e^{\frac{\psi_A + \psi_B - (E_A + E_B)}{\theta}}$$

If $\theta_A = \theta_B$

Oct 21

Properties of the canonical ensemble.

1) Normal properties:

Let us calculate the dispersion in energy.

$$\Delta E = \overline{(E - \bar{E})^2} = \bar{E^2} - \bar{E}^2$$

$$\bar{E} = \int \rho E \, d\tau = \int d\tau \, e^{\frac{\psi - E}{\theta}} E(pq)$$

The following is a useful computational trick: Let us calc.

$$\frac{d\bar{E}}{d\theta} = \int d\tau \left(-\frac{\psi - E}{\theta^2} + \frac{1}{\theta}\frac{\partial \psi}{\partial \theta} \right) \rho E$$

A) $$\frac{d\bar{E}}{d\theta} = \frac{\overline{E^2}}{\theta^2} - \frac{\psi \bar{E}}{\theta^2} + \frac{\bar{E}}{\theta}\frac{d\psi}{d\theta}$$

We have also $\int P d\tau = 1$

$$\frac{d}{d\theta} \| \quad e^{-\psi/\theta} = \int e^{-E/\theta} d\tau$$

$$e^{-\psi/\theta}\left(\frac{\psi}{\theta^2} - \frac{1}{\theta}\frac{d\psi}{d\theta}\right) = \int \frac{E}{\theta^2} e^{-E/\theta} d\tau$$

$$\bar{E} \| \quad \frac{\psi}{\theta^2} - \frac{1}{\theta}\frac{d\psi}{d\theta} = \frac{\bar{E}}{\theta^2}$$

B) $$\frac{\bar{E}\psi}{\theta^2} - \frac{\bar{E}}{\theta}\frac{d\psi}{d\theta} - \frac{\bar{E}^2}{\theta^2} = 0$$

Add A + B

$$\frac{d\bar{E}}{d\theta} = \frac{\overline{E^2} - \bar{E}^2}{\theta^2}$$

$$\Delta E = \theta^2 \frac{d\bar{E}}{d\theta}$$

For an ideal gas $\bar{E} \sim nkT = n\theta$
where n = # of degrees of freedom

$$\frac{d\bar{E}}{d\theta} \sim n$$

$$\frac{\Delta E}{\bar{E}^2} \sim \frac{\theta^2}{n^2\theta^2} \cdot n = \frac{1}{n}$$

or $$\sqrt{\Delta E}/\bar{E} = \frac{1}{\sqrt{n}}$$

Problem: Assume $E = E(p) + E(q)$
Find $\frac{\Delta E_p}{E_p^2}$ and $\bar{E}_p$ for n degrees of freedom.

2) If a thermostat (large heat bath isolated from its surroundings) is microcanonical, then a small subsystem will be canonical.

We have $\bar{E} = n\theta$

$$\delta\theta \sim \frac{\delta \bar{E}}{n}$$

Consider a small subsystem in the center of the bath. Its small change $\delta\theta$ in θ esp to a relatively large change in the average energy of the bath compared to the change in the average energy of the subsystem.

$$\Delta \bar{E}_{SUB} / \Delta E_{BATH} \sim n_{SUB} / n_{BATH}$$

Another way of saying it is to say that the small systems are insensitive to

fluctuations in the energy of the bath. If our small systems are canonical, we are free to choose almost any energy distribution for the bath. In particular, it could have been microcanonical at any one of many E's

3) Minimal Properties

Problem:

$$\bar{H} \equiv \int \rho \ln \rho \, d\tau$$

$$H = \ln \rho$$

a) If $\int \rho \, d\tau = 1$ show $\rho_i = a$ constant minimizes $\bar{H}$

b) If $\int \rho \, d\tau =$ and $\bar{E}$ is given show a canonical distribution makes H a minimum

Perfect Gas

$$\rho = e^{\frac{\psi}{\theta} - \frac{E}{\theta}} = e^{\frac{\psi}{\theta} - \frac{\sum \frac{p^2}{2m}}{\theta}}$$

$$\rho = e^{\psi/\theta} \prod_i e^{-\frac{p_i^2}{2m_i \theta}}$$

ρ is a product of canonical distributions for the individual molecules.

Equipartition Theorem

$$e^{\psi/\theta} \int e^{-E/\theta} d\tau = 1.$$

where $d\tau = dp_1 \dots dq_f$

Integrate by parts with respect to q_i (any coord in phase space)

$$e^{\psi/\theta} \int\int q_i e^{-E/\theta} \Big|_{q_{i\,min}}^{q_{i\,max}} dp_1 \dots dq_{i-1}\, dq_{i+1} \dots dq_f$$

$$- e^{\frac{\psi}{\theta}} \int q_i \left(-\frac{1}{\theta}\frac{\partial E}{\partial q_i}\right) e^{-\frac{E}{\theta}} dp_1 \dots dq_f = 1$$

In many cases the first term will be zero by virtue of the fact that

$$q_i e^{-E/\theta}$$

vanishes at $q_{i\,min}$ and $q_{i\,max}$. This is the case when $q_i = p_x$, $E = \frac{p_x^2}{2m}$ or $q_i = x$, $E \approx \frac{kx^2}{2}$

If the first term is zero, we have left.

$$\int q_i \frac{\partial E}{\partial q_i} = \theta$$

Let $q_i = p_x$ $\quad E = \frac{p_x^2}{2m}$ $\quad \frac{\partial E}{\partial p_x} = \frac{p_x}{m}$

$$\frac{p_x^2}{m} = \theta$$

$$\frac{p_x^2 + p_y^2 + p_z^2}{2m} = \frac{3\theta}{2}$$

We have $\frac{\theta}{2}$ contribution to the energy for each degree of freedom. (for E quadratic in p & q)

Problem: Find gas law and equipartition (if any) for a relativistic gas.

Oct 23

Work: energy transfer to a mechanically described system. A change in the Hamiltonian.

Heat: internal and thermal energy. A change in the distribution in phase space.

The mechanical work done by the members of an ensemble may be taken into account by introducing a parameter (or parameters) which characterize the work done and are the same for all members of the ensemble.

Identification with Thermodynamics

$$E = E(\rho_g V)$$

$$1 = \int \rho \, d\tau = \int e^{\frac{\psi(v) - E(v)}{\theta(v)}} d\tau$$

$$e^{-\psi/\theta} = \int e^{-E/\theta} d\tau$$

Change V by δV

$$e^{-\psi/\theta}\left(-\frac{\delta\psi}{\theta} + \frac{\psi \delta\theta}{\theta^2}\right) = \int e^{-\frac{E}{\theta}} d\tau \left(\frac{E\delta\theta}{\theta^2} - \frac{1}{\theta}\frac{\partial E}{\partial V}\delta V\right)$$

$$\psi \frac{\delta\theta}{\theta} - \delta\psi = \frac{\delta\theta}{\theta}\bar{E} - \delta V \overline{\frac{\partial E}{\partial V}}$$

Let $P = -\left.\overline{\frac{\partial E}{\partial V}}\right|_{\theta\psi} = -\frac{\partial E}{\partial V}$

$$\delta\psi = \frac{\psi - \bar{E}}{\theta}\delta\theta - P\delta V$$

We are tempted to identify this with the thermodynamic equation.

$$\delta A = -S\delta T - P\delta V$$

$A \equiv$ Helmholtz free energy $= U - TS$

$S \equiv$ Entropy

$U \equiv$ Internal Energy

$$A = \Psi$$
$$S = -k(\Psi - \bar{E})/\theta$$
$$T = \theta/k$$

Consider $\rho = e^{\frac{\Psi - E}{\theta}}$

$$\ln \rho = (\Psi - E)/\theta$$
$$\overline{\ln \rho} = (\Psi - \bar{E})/\theta$$

$$S = -k\,\overline{\ln \rho}$$

Computational Trick

Let: $Z = e^{-\Psi/\theta} = \int e^{-E/\theta}\, d\tau$

We can express things in terms of operations on Z

$$A = -\theta \ln Z = -kT \ln Z$$

$$P = -\frac{\overline{\partial E}}{\partial v}\Big/_{\theta\Psi} = -\int \frac{\partial E}{\partial v} e^{\frac{\Psi - E}{\theta}}\, d\tau$$

$$= e^{\Psi/\theta}\, \theta \frac{\partial}{\partial v} \int e^{-E/\theta}\, d\tau \Big|_{\Psi\theta}$$

$$P = kT \frac{1}{Z} \frac{\partial Z}{\partial V} = kT \frac{\partial \ln Z}{\partial V}\Big|_{\theta \psi}$$

Problem: Find C_V, U, S as functions of Z.

$Z = Q$ = partition function or the sum over states

$$Z = \sum_{\text{all states}} e^{-E/kT}.$$

If Z is given the system is solved.

Quantum Mechanics

$$\bar{F}_n = \sum_m F_{nm} \rho_{mn}$$

$$F_{nm} = \int \psi_m F \psi_m \, d\tau$$

$$\rho_{nm} = c_m^* c_n$$

In Q.M., our ensemble is a collection of wave functions. The ensemble average in Q.M. is really a double average,

one over the components of a wave function and another over different wave functions.

$$\overline{\overline{F}} = \sum_m F_{nm} \overline{\rho}_{mn}$$

$\overline{\rho}_{mn}$ = ensemble density matrix and is the average over the ρ^{α}_{mn} associated with ψ^{α}. For N members of the ensemble

$$\overline{\rho}_{mn} = \frac{1}{N} \sum_{\alpha=1}^{N} c_m^*(\alpha)\, c_n(\alpha)$$

$$= \frac{1}{N} \sum_{1}^{N} a_m^{\alpha} a_n^{\alpha} e^{i(\phi_n^{\alpha} - i\phi_m^{\alpha})}$$

The $\overline{\rho}_{nn}$ are real. We choose our ensemble so that the off diagonal elements are zero.

$$\overline{\rho}_{nm} = \delta_{nm} f(n)$$

This implies random phase among members of the ensemble.

$$\bar{E} = \sum_n F_{nn} \bar{\rho}_{nn}$$

Oct 28

$$\bar{\rho}_{nn} = e^{(\psi - E_n)/\theta}$$

$$\bar{E} = \sum_n F_{nn} e^{(\psi - E_n)/\theta}$$

$$\text{Let } Z = \sum_{\text{all states}} e^{-\frac{E_n}{\theta}}$$

Enumerating states

Consider a free particle in a box, $L_x \times L_y \times L_z$

$\psi \sim \sin k_x x \sin k_y y \sin k_z z$

We require ψ to be periodic in L_x, L_y, L_z.

$k_x \cdot L_x = n_x \pi$, etc.



In n-space each lattice point corresponds to a state of the system. Only

positive n have meaning. The total # of states for which $\left(\frac{n_x \pi}{L_x}\right)^2 + \left(\frac{n_2 \pi}{L_2}\right)^2 + \left(\frac{n_y \pi}{L_y}\right)^2 \leq R^2$ is roughly equal to $\frac{1}{8}$ the volume of an ellipsoid of axes: $L_y k/\pi$, $L_x k/\pi$, $L_2 k/\pi$

$$\text{Total \# states} = \frac{1}{8} \int d\bar{n}$$

$$= \frac{1}{8} \frac{4}{3} \pi n_{x_{max}} n_{y_{max}} n_{z_{max}}$$

$$= \frac{1}{8} \frac{4}{3} \pi \left(k^3 L_x L_y L_z / \pi^3 \right)$$

This gives the total # of states up to a fixed energy ($E \leq \hbar c k$)

$$k = p/\hbar$$

$$\# \text{ states } (E \leq \hbar c k) = \frac{1}{8\pi^3} \frac{4\pi}{3} \frac{p^3}{\hbar^3} L_x L_y L_z$$

$$\rho \text{ in phase space} = \frac{1}{8\pi^3 \hbar^3} = \frac{1}{h^3}$$

$$dn = \frac{d\bar{p}\, d\bar{r}}{h^3}$$

For N particles

$$dn = d\bar{p}_1 \ldots d\bar{p}_N\, d\bar{q}_1 \ldots d\bar{q}_N / h^{3N}$$

Partition Function

$$Z = \sum_{\text{all states}} e^{-\frac{E_i}{\theta}}$$

Consider systems in which element (molecule) of an ensemble element (flask of gas) has the same Hamiltonian.

The energy of the i^{th} flask

$$E_i = \epsilon_1 + \epsilon_2 + \epsilon_3 + \dots$$

where ϵ_n is the energy of the n^{th} molecule in the gas. We may write symbolically

$$E_i = \sum_n \epsilon_n^i \quad \text{count all } \overset{\text{molecules}}{\cancel{\text{states}}}$$

or

$$E_i = \sum_n \epsilon_n k_n^i \quad \text{count all states}$$

where k_n^i gives the # of molecules in flask i occupying the energy level ϵ_n.

$$Z = \sum_i e^{-\sum_n \epsilon_n^i/\Theta}$$

$$= \sum_i e^{-(\epsilon_1^i + \epsilon_2^i + \epsilon_3^i + \ldots)/\Theta}$$

$$= \sum_i e^{-\frac{\epsilon_1^i}{\Theta}} e^{-\frac{\epsilon_2^i}{\Theta}} e^{-\frac{\epsilon_3^i}{\Theta}} \cdots e^{-\frac{\epsilon_m^i}{\Theta}}$$

Since all molecules have identical energy states ϵ, the sum over the ensemble members is merely a sum over all combination of the same set of ϵ. We may therefore write

$$Z = \left(\sum_{\substack{\text{all states of} \\ \text{on molecule } i}} e^{-\frac{\epsilon_i}{\Theta}} \right)^n$$

n = # of molecules

This formula is valid as long as the molecules can be distinguished unambiguously. It is always o.k. in classical mechanics and o.k. in Q.M. if there are no diffraction effects.

Oct 30

Recapitulation:

We wrote last time.

$$Z = \sum_i \prod_\alpha e^{\epsilon_\alpha / \theta}$$

If we use the notation

$$E_i = \sum_{\text{all}\,\alpha} n_\alpha^i \epsilon_\alpha$$

where ϵ_α represents a possible state of a molecule and n_α^i represents the # of molecules in the i^{th} flask occupying the state ϵ_α, we may write

$$Z = \sum_{\substack{i \\ \text{all configurations}}} \frac{N!}{n_1^i! n_2^i! \cdots} e^{-\sum_{\text{all}\,\alpha} n_\alpha^i \epsilon_\alpha / \theta}$$

$$= \left(\sum_{\substack{\text{all molecular} \\ \text{states}}} e^{-\epsilon_\alpha / \theta} \right)^N$$

N = total # of molecules

This result applies if the particles can be distinguished unambiguously from one another.

In Q. M. we have:

$$\langle O \rangle = \int \psi^* O \psi \, d\tau$$

Let P_{ab} be the permutation operator

$$P_{ab} \psi(ab) = \psi(ba)$$

We require

$$\langle O \rangle = \int (P_{ab} \psi)^* O P_{ab} \psi \, d\tau$$

This means that in Q M particles a & b are indistinguishable from one another. It also implies

$$\begin{cases} P_{ab} \psi = \psi \\ P_{ab} \psi = -\psi \end{cases}$$

(There are other operators which can accomplish our result but they have no meaning in physics)

In nature:

spin: $\frac{1}{2}$ integer esp (−), antisymmetric,
Pauli Exclusion principle, Fermic Dirac Stat.

spin: integer esp (+) symmetric,
Bose Einstein Stat. (only light quanta)

The fact that formally the particles are indistinguishable in Q M does not mean that if they are far apart there is much danger of their getting mixed up. We have:

$$\Psi = (\Psi_1 + \Psi_2)/\sqrt{2}$$

$$(\Psi^* \circ \Psi) = \tfrac{1}{2}(\Psi_1^* \circ \Psi_1) + \tfrac{1}{2}(\Psi_1^* \circ \Psi_2) + \tfrac{1}{2}(\Psi_2^* \circ \Psi_1) + \tfrac{1}{2}(\Psi_2^* \circ \Psi_2)$$

If the wave functions Ψ_1 & Ψ_2 do not overlap much, the cross terms are zero and we get just the result we would have had we considered the electron separately.

Suppose we have a system of particles which interact weakly

$$\Psi(q_1 q_2 q_3 \ldots) = \psi(q_1)\psi(q_2)\psi(q_3)\ldots$$

Obviously if all the ψ's are alike interchanging two particles does nothing to Ψ. This is O.K. if Ψ obeys bose einstein statistics but we must be careful not to count the same state more than once. If Ψ obeys Fermi Dirac statistics it is obvious that no two particles can have exactly the same wave functions — since the exclusion principle.

We shall now apply our Q.M. results to our statistical problem of finding Z. In finding Z we count as different states permutations of the various

molecules among the different energy levels. Q.M. tells us this is wrong. We have only one state. To correct our result we must divide by the # of such permutations.

$$Z = \sum_i \frac{n_1^i! n_2^i! n_3^i! \ldots}{N!} \frac{N!}{n_1^i! n_2^i! n_3^i! \ldots} e^{-\sum_\beta \frac{n_\beta^i \epsilon_\beta}{\theta}}$$

If the # of states is large there will in general be 1 or 0 molecules per state. Hence the n_α^i's = 1

$$Z = \frac{1}{N!} \sum_{\substack{i \\ \text{flasks}}} \frac{N!}{n_1^i! n_2^i! \ldots} e^{-\sum_{\substack{\beta \\ \text{states}}} n_\beta^i \epsilon_\beta / \theta}$$

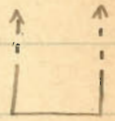
$$= \frac{1}{N!} \left(\sum_{\substack{\alpha \\ \text{all molecular} \\ \text{states.}}} e^{-\epsilon_\alpha / \theta} \right)^N$$

$$= \frac{1}{N!} \sum_{\substack{i \\ \text{flasks}}} e^{-\sum_{\substack{\alpha \\ \text{mol.}}} \epsilon_\alpha^i / \theta}$$

———— o ————

Application to a Perfect Gas

$$\epsilon_\alpha = p^2/2m + V_{box}$$



$$Z = \frac{1}{N!}\left\{\int d\bar{p}\, e^{-p^2/2mkT} \int d\bar{r}\, e^{-V/kT}\right\}^N$$

$$= \frac{1}{N!}\left\{\int p^2 dp\, 4\pi e^{-p^2/2mkT} \int_{box} d\bar{r}\right\}^N$$

$$= \frac{1}{N!}\, V^N \left\{\int p^2 dp\, 4\pi e^{-p^2/2mkT}\right\}^N$$

$$= \frac{1}{N!}\, V^N \left(\frac{m}{2}\sqrt{2m\pi kT}\right)^N$$

$$\ln Z = N \ln V - \ln N! + N \ln\left(\frac{m}{2}\sqrt{2m\pi kT}\right)$$

$$\text{Pressure} = kT \frac{\partial \ln Z}{\partial V}$$

$$= kT \frac{N}{V}$$

$$PV = (Nk)T = RT$$

For an ideal gas:

$$\ln Z = n \ln V - \ln n! + n \ln \frac{mkT}{2} + \frac{n}{2} \ln 2\pi m kT$$

Problem:
Find $\bar{E}$ C_v S. Investigate S as $T \to 0$

Pure Internal Motion

$$H = H_{cm} + T_{int} + V$$

In our case $H_{cm} = 0$

$$H = T_{int} + V = \frac{p^2}{2m} + \frac{k}{2} q^2$$

Problem:
Evaluate C_v for a set of classical SHO. The result is n.g. It gives a constant C_v.

C_v for a set of quantized oscillators.

$$E = (n + \tfrac{1}{2})\, h\nu$$

$$Z = \sum_n e^{-\frac{h\nu(n+\frac{1}{2})}{kT}} = e^{-\frac{h\nu}{2kT}} \sum_n e^{-\frac{h\nu n}{kT}}$$

$$= e^{-\frac{h\nu}{2kT}} / (1 - e^{-\frac{h\nu}{kT}})$$

If the oscillators are distinguishable and have a fundamental frequency, ν_j

$$Z = \prod_j Z_j = \prod_j e^{-h\nu_j/2kT} / (1 - e^{-h\nu_j/kT})$$

$$\ln Z = -\sum_j \left(\frac{h\nu_j}{2kT} + \ln(1 - e^{-\frac{h\nu_j}{kT}}) \right)$$

[In general $\sum_j \to \int p(\nu)\, d\nu$]

Einstein Theory of Specific Heats.

We consider a solid of N particles as a collection of $3N$ identical harmonic oscillators.

$$\ln Z = -3N\left(\frac{h\nu}{2kT} + \ln\left(1 - e^{-\frac{h\nu}{kT}}\right)\right)$$

$$E = -\frac{\partial \ln Z}{\partial\left(\frac{1}{kT}\right)} = \frac{3Nh\nu}{2} + \frac{h\nu e^{-\frac{h\nu}{kT}}}{1 - e^{-h\nu/kT}}$$

$$E = 3N\cdot\left(\frac{h\nu}{2} + \frac{h\nu}{e^{h\nu/kT} - 1}\right)$$

$$\frac{h\nu}{kT} << 1$$

$$= 3N\left(\frac{h\nu}{2} + kT\right) \sim 3NkT$$

We could have obtained this last result from equipartition: each of the 3 "particle oscillators" has 2 quad terms - $3 \cdot 2 \cdot \frac{1}{2}kT = 3kT$ per particle.

Problem: Calc C_v per mole. Plot as a function of $h\nu/kT$.

Einstein's theory assumes no interaction between the oscillators.

Debye Theory of Specific Heats.

Instead of considering the vibrations of the individual molecules, Debye approximated the modes of vibration of a crystal by those of an isotropic continuum. Only as many modes are considered as there are degrees of freedom of the atoms in the crystal.

$$\psi = \sin \frac{n_x \pi x}{L_x} \sin \frac{n_y \pi y}{L_y} \sin \frac{n_z \pi z}{L_z}$$

$$\nu^2 = c^2 \left(\frac{n_x^2}{4L_x^2} + \frac{n_y^2}{4L_y^2} + \frac{n_z^2}{4L_z^2} \right)$$

# of states up to ν_m

$$\int_0^{\nu_m} P(\nu) d\nu = \frac{1}{8} \frac{4}{3} \pi \left(\frac{8 L_x L_y L_z}{c^3} \right) \nu_m^3$$

For a given direction of propagation, we can have one compressional wave and two transverse waves.

$$\therefore \quad N(v_m) = \frac{4}{3}\pi V v_m^3 \left(\frac{1}{c_L^3} + \frac{2}{c_T^3} \right)$$

This must equal # of degrees of freedom for crystal

$$= 3Nn$$

where N = # of molecules in V

n = # of atoms per molecule.

$$P(v)dv \doteq V 4\pi v^2 dv \left(\frac{1}{c_L^3} + \frac{2}{c_T^3} \right) = 3Nn \frac{3v^2}{v_m^3} dv$$

$$\ln Z = -\sum_j \left(\frac{h\nu_j}{2kT} + \ln\left(1 - e^{-h\nu_j/kT}\right) \right)$$

$$\approx -\int_{v_{min}}^{v_m} P(v)dv \left(\frac{h\nu}{2kT} + \ln\left(1 - e^{-h\nu/kT}\right) \right)$$

$$= -\frac{9Nn}{v_m^3} \int_{v_{min}}^{v_m} v^2 dv \left(\quad " \quad \right)$$

v_{min} is small and can be replaced by zero.

$$\bar{E} = -\frac{\partial \ln Z}{\partial\left(\frac{1}{kT}\right)}$$

$$= \frac{9Nn}{v_m^3} \left[\frac{h\nu}{8}^4 + \int_0^{v_m} v^2 dv \, \frac{h\nu e^{\frac{h\nu}{kT}}}{1 - e^{-h\nu/kT}} \right]$$

$$C_v = \frac{\partial \bar{E}}{\partial T} = \frac{9Nn}{v_m^3}\int_0^{v_m} v^2 dv \frac{e^{\frac{h\nu}{kT}}}{(e^{+h\nu/kT}-1)^2}\frac{(h\nu)^2}{kT^2}$$

Let $x = h\nu/kT$

$x_m = h\nu_m/kT = \frac{k\theta}{kT}$

where $\theta \equiv$ Debye temperature.

$$C_v = \frac{9Nn}{v_m^3} k\left(\frac{kT}{h}\right)^3 \int_0^{\theta/T} dx\, x^4 \frac{e^x}{(e^x-1)^2}$$

$$= 9Nnk\left(\frac{T}{\theta}\right)^3 \int_0^{\theta/T} e^x x^4 dx/(e^x-1)^2$$

$$= 3Rn\, f\left(\frac{\theta}{T}\right) \quad \text{per mole}$$

$$f\left(\frac{\theta}{T}\right) \equiv 3\left(\frac{T}{\theta}\right)^3 \int_0^{\theta/T} e^x x^4 dx/(e^x-1)^2$$

As $\frac{\theta}{T} \to 0 \quad f\left(\frac{\theta}{T}\right) = 1$

$C_v = 3Rn$ This is the classical Delong Petit law.

For low temperature $\frac{\theta}{T} \gg 1$

$$f\left(\frac{\theta}{T}\right) = \frac{3}{x^3}\underbrace{\int_0^{\infty} e^{-x} x^9 dx}_{\Gamma(5)} \sim \frac{1}{x^3}$$

In the derivation we have assumed the velocity of sound independent of the frequency.

The Debye specific heats are excellent - if θ is determined empirically - for isotropic crystals composed of not too complicated molecules.

Influence of Fermi and Bose Statistics

Gas degeneracies

$$P_k = e^{\Psi - E_k/\theta}$$

$$E_k = \sum_n e^k_n$$

If we assume no interaction between particles, the prob of having a single particle in the i^{th} state is

$$P_i = e^{-\epsilon_i/\theta} / \left(\sum_i e^{-\epsilon_i/\theta}\right)$$

$\left(\sum_i e^{-\epsilon_i/\theta}\right)$ is the normalization factor.

$$\sum_i P_i = 1$$

Problem: If p_i is the prob of having a particle in state, i, and there are N particles, find the mean # of particles in state, i. The prob of having n particles in state, i is:

$$w_n^i = p_i^n (1-p_i)^{N-n} \frac{N!}{n!(N-n)!}$$

$$\bar{n}_i = N p_i = \left(\frac{N}{\sum e^{-\epsilon_i/\theta}}\right) e^{-\epsilon_i/\theta} = C N e^{-\epsilon_i/\theta}$$

Nov 11

The prob of n particles in a state is $\propto e^{-n\epsilon_i/\theta}$. The prob of a given distribution is:

$$P(n_1, n_2, n_3 \ldots) = e^{\psi/\theta - \sum_k n_k \epsilon_k/\theta}$$
$$= e^{\psi/\theta - n_k \epsilon_k/\theta - \sum_{\alpha \neq k} n_\alpha \epsilon_\alpha/\theta}$$

To find $P(n_k)$ we must sum over all distributions for which $n_k = n_k$

$$P(n_k) = e^{\psi/\theta - \frac{n_k \epsilon_k}{\theta}} \sum_{\substack{\text{all dist} \\ \text{of } n_\alpha}} e^{-\sum_{\alpha \neq k} n_\alpha \epsilon_\alpha / \theta}$$

The sum is not a free one and in practice this is not a good way to find $P(n_k)$

Examples of different kinds of Statistics

3 Particles a b c

3 Energy states ϵ_1 ϵ_2 ϵ_3

Classical Statistics.

weight	ϵ_1	ϵ_2	ϵ_3	# permutations
$\frac{1}{27}$	abc			1
		abc		1
		c	abc	1
	ab	b	0	3
		a		
	ab	0	c	3
			b	
			a	
	0	ab	c	3
$\frac{1}{9}$	0	c	ab	3
	a	bc	0	3
	a	0	bc	3
$\frac{2}{9}$	a	b	c	6
				27

Bose Einstein Statistics

Weight	ϵ_1	ϵ_2	ϵ_3	
$\frac{1}{10}$	abc			1
		abc		1
per state			abc	1
	ab	c	0	1
	ab	0	c	1
	0	ab	c	1
	0	c	ab	1
	a	bc	0	1
	a	0	bc	1
	a	b	c	1
				$\frac{1}{10}$

a b c indistinguishable.

Fermi Dirac Statistics

One particle in a given state.

ϵ_1	ϵ_2	ϵ_3
a	b	c

The partition function

$$Z = \sum_{\substack{\text{allowed} \\ \text{states of system}}} \frac{n_1! n_2! \ldots}{N!} e^{-\sum_{\text{all molecules}} \epsilon_\alpha / kT}$$

$$Z_{\text{Max Bol}} = \frac{1}{N!} \left(\sum_{\substack{\alpha \\ \text{all mol} \\ \text{states}}} e^{-\epsilon_\alpha / kT} \right)^N \checkmark$$

$$Z_{BE} = \sum_{\text{all } n_\alpha} e^{-\sum_{\text{mol states}} n_\alpha \epsilon_\alpha / kT}$$

$$Z_{FD} = \sum_{n_\alpha = 0}^{1} e^{-\sum_{\text{mol states}} n_\alpha \epsilon_\alpha / kT}$$

Method of Counting states due to Darwin and Fowler

Bose Einstein: Consider the following infinite product:

$$F_{BE} = \prod_{i=1}^{\#\text{states } \epsilon_i} \left(1 + z e^{-\epsilon_i/kT} + z^2 e^{-2\epsilon_i/kT} + z^3 e^{-3\epsilon_i/kT} + \ldots\right)$$

For a system of N particles the coefficient of $z^N = Z_{BE}$

Fermi Dirac: Consider:

$$F_{FD} = \prod_{i=1}^{\#\text{states } \epsilon_i} \left(1 + z e^{-\epsilon_i/kT}\right)$$

The coefficient of $z^N = Z_{FD}$

To evaluate these products we introduce the Grand canonical ensemble.

$$Z_{GC} = \sum_{i\,N} e^{-E_i/\theta - \mu N}$$

$$= \sum_{i\,N} e^{-\sum_l \{n_l^i \epsilon_l/\theta + \mu n_l^i\}}$$

$$= \sum_{i\,N} e^{-\sum_l n_l^i \left(\frac{\epsilon_l}{kT} + \mu\right)}$$

$$= F(z=1)$$

$$Z_{BEGC} = \prod_{i=1}^{\infty} \frac{1}{\left(1 - e^{-(\epsilon_i/kT + \mu)}\right)}$$

$$Z_{FDGC} = \prod_{i=1}^{\infty} \left(1 + e^{-(\epsilon_i/kT + \mu)}\right)$$

These results will be good if we can show that the fluctuations in N are not large.

$$\bar{E} = -\frac{\partial \ln Z}{\partial\left(\frac{1}{kT}\right)}$$

$$\bar{E}_{BE} = -\frac{\partial}{\partial(\frac{1}{kT})} - \sum_i \ln\left(1 - e^{-(\frac{\epsilon_i}{kT} + \mu)}\right)$$

$$= \sum_i \frac{\epsilon_i e^{-(\frac{\epsilon_i}{kT} + \mu)}}{(1 - e^{-(\ )})}$$

$$= \sum_i \epsilon_i / (e^{\frac{\epsilon_i}{kT} + \mu} - 1)$$

$$= \sum_i \epsilon_i \bar{n}_i$$

where $\bar{n}_i \equiv \dfrac{1}{(e^{\epsilon_i/kT + \mu} - 1)}$

To find μ we impose the condition

$$\bar{N} = \sum_i \bar{n}_i = \sum \frac{1}{(e^{\epsilon_i/kT + \mu} - 1)}$$

Note that if the energy levels are very close and numerous, $\bar{n}_i$ will be small. This means $e^{-(\frac{\epsilon_i}{kT} + \mu)} \sim 0$ and $\bar{E}_{BE}$ reduces to the classical $\bar{E}$.

$$\bar{E}_{FD} = \sum_i \frac{\epsilon_i e^{-(\frac{\epsilon_i}{kT} + \mu)}}{(1 + e^{-(\ )})}$$

$$= \sum_i \epsilon_i / (e^{\epsilon_i/kT + \mu} + 1)$$

$$\bar{E}_{MB} = \sum_i \epsilon_i \Big/ e^{\frac{\epsilon_i}{kT} + \mu}$$

Noo 13

We have:

$$\bar{E} = \sum_i \epsilon_i \Big/ \left(e^{\mu + \frac{\epsilon_i}{kT}} \begin{matrix} +1 \\ 0 \\ -1 \end{matrix} \right\} \begin{matrix} FD \\ MB \\ BE \end{matrix}$$

$$\bar{n}_i \equiv 1 \Big/ \left(e^{\mu + \frac{\epsilon_i}{kT}} \begin{matrix} +1 \\ 0 \\ -1 \end{matrix} \right\} \begin{matrix} FD \\ MB \\ BE \end{matrix}$$

$$\bar{N} = \sum_i \bar{n}_i$$

$$= \sum_i 1 \Big/ \left(e^{\mu + \frac{\epsilon_i}{kT}} + \delta \right)$$

where $\delta = \begin{matrix} +1 \\ 0 \\ -1 \end{matrix} \Big\} \begin{matrix} FD \\ MB \\ BE \end{matrix}$

Let us compute the dispersion in $\bar{N}$.

$$\overline{N^2} - \bar{N}^2 = \frac{\partial^2}{\partial \mu^2} \ln Z_{GC}$$

Let us prove this:

$$Z_{GC} = \sum_{iN} e^{-(\mu N + \frac{E_i}{\theta})}$$

$$\frac{\partial Z_G}{\partial \mu} = -\sum_{iN} N e^{-(\mu N + \frac{E_i}{\theta})}$$

$$\frac{1}{Z_G}\frac{\partial Z_G}{\partial \mu} = \frac{\partial \ln Z_G}{\partial \mu} = -\frac{\sum N e^{-(\ )}}{\sum e^{-(\ )}}$$

$$\frac{\partial^2 \ln Z_G}{\partial \mu^2} = \frac{\sum N^2 e^{-(\ )}}{\sum e^{-(\ )}} - \frac{\sum N e^{-(\ )} \sum N e^{-(\ )}}{(\sum e^{-(\ )})^2}$$

$$= \bar{N^2} - \bar{N}^2$$

The above definition of $\bar{N}$ can be shown to be equivalent to that already formulated by using the infinite product definition of Z.

$$\ln Z_{GBE} = \sum_i -\ln\left(1 - e^{-(\mu + \frac{\epsilon_i}{kT})}\right)$$

$$\frac{\partial}{\partial \mu} \ln Z_{GBE} = -\sum \frac{1}{(e^{\mu + \frac{\epsilon_i}{kT}} - 1)}$$

$$\frac{\partial^2}{\partial \mu^2} \ln Z_{GBE} = \sum \frac{e^{\mu + \frac{\epsilon_i}{kT}}}{(e^{\mu + \frac{\epsilon_i}{kT}} - 1)^2}$$

$$= \sum_i (\bar{n}_i)^2 e^{\mu + \frac{\epsilon_i}{kT}}$$

$$e^{\mu + \frac{\epsilon_i}{kT}} = \frac{1}{\bar{n}_i} + 1$$

$$\overline{N^2} - \bar{N}^2 = \sum_i \bar{n}_i (1 + \bar{n}_i)$$

$$\frac{\overline{N^2} - \bar{N}^2}{\bar{N}^2} = \frac{1}{\bar{N}} + \frac{\sum_i \bar{n}_i^2}{\bar{N}^2}$$

If $n_i \sim 1$ $\quad \sum \bar{n}_i^2 \sim \bar{N}$

$$\frac{\overline{N^2} - \bar{N}^2}{\bar{N}^2} \approx \frac{2}{\bar{N}} \qquad BE$$

This means that for large N the fluctuations are certainly small if the states are not crowded.

$$\frac{\overline{N^2} - \bar{N}^2}{\bar{N}^2} = \frac{1}{\bar{N}^2} \sum_{i=0}^{1} \bar{n}_i (1 - \bar{n}_i) \qquad FD$$

Note that the dispersion is the same whether we consider the distribution of filled or empty states for an FD distribution.

$$\frac{\overline{N^2} - \bar{N}^2}{\bar{N}^2} = \frac{1}{\bar{N}} \qquad MB$$

$$\bar{n}_i = \sum_{n_i} P(n_i)\, n_i$$

$$\bar{n}_i = 1/(e^{\alpha + \frac{\epsilon_i}{kT}} + \delta)$$

For F.D.

$$\bar{n}_i = P(0_i)\cdot 0_i + P(1_i)\, 1_i$$

$$P(1_i) = 1/(e^{\alpha + \frac{\epsilon_i}{kT}} + 1)$$

$$P(0_i) = 1 - P(1_i) = \frac{e^{\alpha + \frac{\epsilon_i}{kT}}}{(e^{\alpha + \epsilon_i/kT} + 1)}$$

$$\bar{n}_i^2 = \sum_{n_i} P(n_i)\, n_i^2$$

$$= P(1_i) = \bar{n}_i$$

$$\frac{\bar{n}_i^2 - \bar{n}_i^2}{\bar{n}_i^2} = \frac{1}{\bar{n}_i} - 1 \qquad F\,D$$

$$\left\{ \begin{array}{ll} = \dfrac{1}{\bar{n}_i} & M\,B \\ = \dfrac{1}{\bar{n}_i} + 1 & B\,E \end{array} \right\}$$

The following expression for $P(n_i)$ works for FD or BE

$$P(n_i) = e^{-(\mu + \frac{\epsilon_i}{kT})n_i} \Big/ \sum_{n_i} e^{-(\mu + \frac{\epsilon_i}{kT})n_i}$$

For high temperatures, all the distributions approach the MB distribution.

Nov 18

Ref Mayer Chap 16.

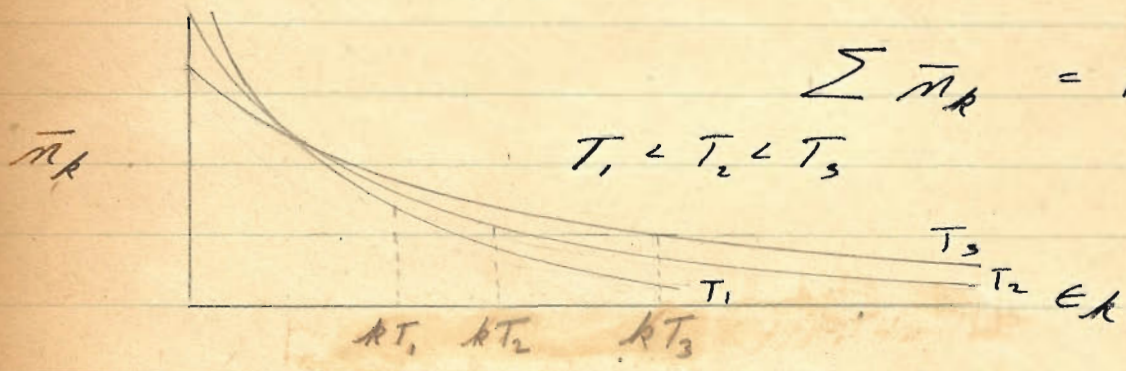
$$\bar{n}_k = 1/(e^{(\mu + \frac{\epsilon_k}{kT})} + \delta)$$

At high temperatures $\bar{n}_k << 1$ and $e^{(\mu + \frac{\epsilon}{kT})} >> 1$ and we can neglect the δ, i.e. the Fermi Dirac and Bose Einstein distributions approach the Maxwell distribution.

Low Temperatures

M.B. $\bar{n}_k = e^{-(\mu + \frac{\epsilon_k}{kT})}$

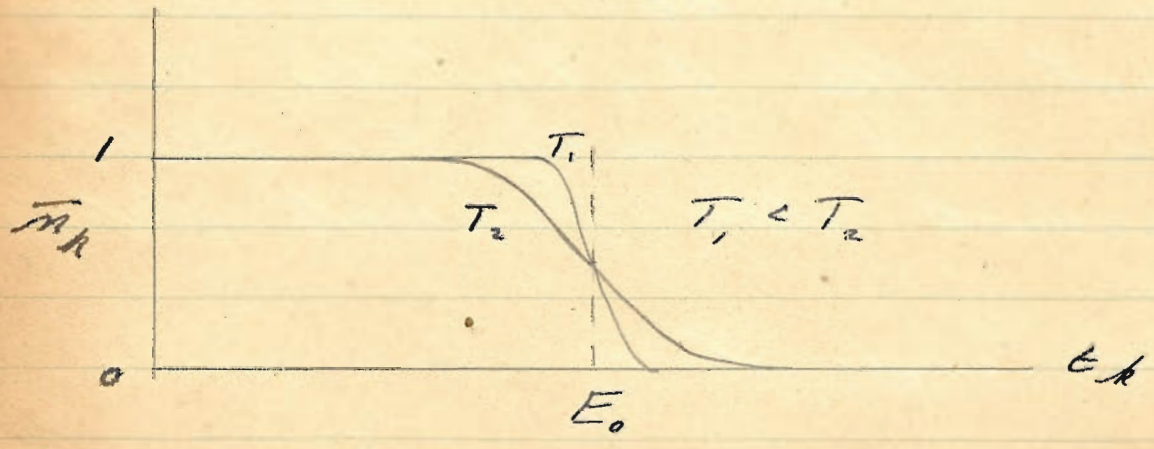
$\sum \bar{n}_k = \bar{N}$



At low temperature the particles tend to crowd into the lowest states.

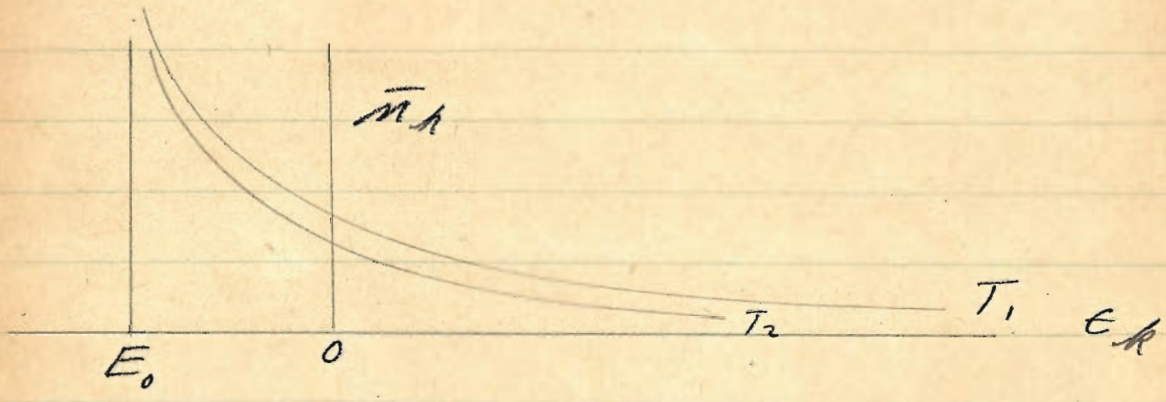
F.D. $\bar{n}_k = 1/(e^{(\mu + \frac{\epsilon_k}{kT})} + 1)$

$= 1/(e^{(\epsilon_k - E_0)/kT} + 1)$



B. E. $\bar{n}_k = 1/(e^{(\epsilon_k - E_0)/kT} - 1)$

$e^{(\epsilon_k - E_0)/kT} > 1$ or $\bar{n}_k$ will be negative. This means $(\epsilon_k - E_0) > 0$ or $\epsilon_k > E_0$. Since ϵ_k may be arbitrarily close to zero $E_0 \leq 0$



Fermi Dirac Cold Gas.

$$P(E)dE = 2 \cdot \frac{4\pi p^2}{h^3} \frac{dp}{dE} dE \cdot V$$

The factor 2 enters because the energy states for particles having spin $1/2$ are doubly degenerate. (In general $g = (2s+1)$)

$$N = \sum_k \bar{n}_k \rightarrow \int_0^\infty n(E) P(E)\, dE$$

$$= \int_0^{p_0} 2 \frac{4\pi p^2}{h^3} dp\, V = \frac{V}{3\pi^2}\left(\frac{p_0}{\hbar}\right)^3$$

Since for a FD gas $n(E) = \begin{cases} 1 & p < p_0 \\ 0 & p > p_0 \end{cases}$

In the non rel limit:

$$E = \frac{p^2}{2m}$$

$$\bar{E} = \int_0^{E_0} E\, n(E) P(E) dE = \int_0^{p_0} 2 \frac{4\pi p^2}{h^3} \frac{p^2}{2m} dp\, V$$

$$= \frac{p_0^5}{5} \frac{8\pi}{2m h^3} V = \frac{p_0^3}{\hbar^3} \frac{1}{10 m \pi^2} p_0^2 V$$

$$= N \frac{3\pi^2}{V} \frac{1}{10 m \pi^2} p_0^2 V$$

$$= \frac{3}{10} \frac{N}{m} p_0^2 = \frac{3}{5} N E_0$$

$$= \frac{3}{10} \frac{N}{m} \left\{ \frac{N 3\pi^2 \hbar^3}{V} \right\}^{2/3}$$

$$= \frac{3}{10} N (3\pi^2 \hbar^3)^{2/3} \frac{\rho^{2/3}}{m}$$

76 where $\rho = \frac{N}{V}$ = particle density.

Pressure: $p = -\left.\frac{\partial A}{\partial V}\right|_T$

where $A = E - TS$

At $T = 0$

$$p = -\left.\frac{\partial E}{\partial V}\right|_{T=0}$$

$$= \frac{3}{10}\frac{N}{m}(3\pi^2\hbar^3)^{2/3}\frac{2}{3}\rho^{5/3}/N$$

$$= \frac{1}{5}(3\pi^2\hbar^3)^{2/3}\frac{\rho}{m}^{5/3}$$

$$= \frac{2}{3}\frac{E}{V}$$

Nov 20

Problem: Find E & p for a cold Fermi gas in the extreme rel limit $p_0 \gg m_0 c$

Ref: Chandrasekhar: Stellar Structure
Fowler.

It is a fair approximation to regard an atom (or nucleus) as a Fermi Cold Gas in a

box the size of the atom.

Problem: Find E_0 for
a) An atom
b) A nucleus
Treat as a perfect gas in a box.

Bose Einstein Hot Gas

The behavior of a photon gas is like that of a B.E. hot gas.

Problem: Consider the EM field in a cavity as a set of SHOs. The oscillators are distinguishable and have quantum states $(n+\frac{1}{2})h\nu_i$ where ν_i is the frequency of the i^{th} mode of the cavity.

(See Einstein & Debye Specific Heat)

BE Hot Gas

Consider a perfect gas of photons

$$\bar{n}_k = 1/(e^{\mu + \epsilon_k/kT} - 1)$$

$$\rho(E)dE = 2 \cdot \frac{4\pi p^2}{h^3} \frac{dp}{dE} dE V$$

The factor 2 takes care of the 2 directions of polarization. Since photons move with the speed of light,

$$p = h\nu/c = \frac{E}{c}$$

$$n(E)\rho(E)dE = \frac{8\pi}{h^3} \frac{(h\nu)^2}{c^2} \frac{1}{c} d(h\nu) V \cdot \left\{ \frac{1}{e^{\mu + h\nu/kT} - 1} \right\}$$

$$n(\nu)d\nu = \frac{8\pi}{c^3} \frac{\nu^2 d\nu}{e^{\mu + h\nu/kT} - 1}$$

$$E(\nu)d\nu = \frac{8\pi}{c^3} \frac{h\nu^3 d\nu}{e^{\mu + h\nu/kT} - 1}$$

Evaluation of μ is somewhat

difficult. The # of quanta is not fixed but depends on the temperature. Large deviations in the # of quanta implies that $\mu \to 0$. Another way of fixing μ is to go to the classical limit, Rayleigh Jeans Law. This is obtained from MB distribution and equipartition which assigns $\frac{1}{2}kT$ to each degree of freedom.

$$E_{cl}(\nu)d\nu = \frac{8\pi\nu^2 d\nu}{c^3} \cdot 2 \cdot \frac{kT}{2}$$

Let us assume that in the classical limit of high T we can expand $e^{\mu + h\nu/kT}$

$$E(\nu)d\nu = \frac{8\pi\nu^2}{c^3} h\nu d\nu \frac{1}{(1+\mu+\frac{h\nu}{kT}-1)}$$

This approaches the classical limit as $\mu \to 0$.

F.D. distribution: degeneracy

Let

$$\delta = \frac{E_{FD}}{E_{CL}} \sim \frac{E_0}{kT}$$

If δ is large the degeneracy of the levels is important.
If δ is small the degeneracy is unimportant.

$$\delta \sim \frac{p_0^2}{\bar{p}_{rms}^2}$$

$$p_0^2 \sim \rho^{2/3}, \quad = \frac{1}{(\text{volume/particle})^{2/3}}$$

$$= \frac{1}{(\delta x^3)^{2/3}} = \delta x^{-2}$$

where δx is the mean particle spacing.

Suppose the momentum of a particle is known with an accuracy of just the momentum

$$\Delta x \, \bar{p}_{rms} \sim \hbar$$

$$\bar{p}_{rms}^2 \sim \hbar^2 / \Delta x^2$$

For comparison with p_0^2 the

classical momentum must be measured on the scale of h.

$$\delta \sim \left(\frac{\Delta x}{\delta x}\right)^2$$

Where Δx is the uncertainty in the position of the molecule due to a definite temperature momentum and δx is the molecular spacing.
A cold gas means a low momentum hence a large Δx (wave packet). The degeneracy is important in this case.

Nov 25

Typical E_0 for condensed matter.

Electrons 100 kT at room temp
Atoms or Mol. $\frac{1}{10}$ kT

For a gas at NTP 10^{-3} kT

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From this we see that the degeneracy is important only for the electron gas.

Cold Bose Einstein Gas

$$\bar{n}_k = 1/(e^{(\epsilon_k + E_0)/kT} - 1)$$

where $E_0 \geq 0$ and $\bar{n}_k \geq 0$

$$\bar{n}_k = \sum_1^\infty e^{-n(\epsilon_k + E_0)/kT}$$

$$\bar{N} = \sum \bar{n}_k \rightarrow \int_0^\infty \frac{4\pi p^2 dp}{h^3} dE \, dE \cdot V \sum_1^\infty e^{-n(\epsilon + E_0)/kT}$$

$$p^2 = 2mE$$

$$p^2 dp = m\sqrt{2mE}\, dE$$

$$\bar{N} = \int_0^\infty V\left(\frac{2m}{h^2}\right)^{3/2} 2\pi \sum E^{1/2} e^{-n(E+E_0)/kT} dE$$

$$= V\left(\frac{2m}{h^2}\right)^{3/2} 2\pi \sum_1^\infty \int_0^\infty E^{\frac{1}{2}} e^{-n\frac{(E+E_0)}{kT}} dE$$

$$= V\left(\frac{2mkT}{h^2}\right)^{3/2} 2\pi \sum_1^\infty e^{-\frac{nE_0}{kT}} \frac{1}{n^{3/2}} \int_0^\infty x^{\frac{1}{2}} e^{-x} dx$$

$$\bar{N} = V \cdot \left(\frac{2\pi m k T}{h^2}\right)^{3/2} \sum_1^\infty \frac{e^{-n\frac{E_0}{kT}}}{n^{3/2}}$$

$$\sum_1^\infty \frac{e^{-n\frac{E_0}{kT}}}{n^{3/2}} = \left(\frac{N}{V}\right)\left(\frac{h^2}{2\pi m k T}\right)^{3/2}$$

In the high temperature case, $\bar{n}_x \ll 1$, E_0/kT large. We need consider only the first term in the sum.

$$e^{-E_0/kT} = \left(\frac{N}{V}\right)\frac{h^3}{(2\pi m k T)^{3/2}}$$

This is the classical result for high T.

In the low temperature case, $E_0/kT \to 0$

$$\sum_1^\infty \frac{1}{n^{3/2}} \geq \sum_1^\infty \frac{e^{-n E_0/kT}}{n^{3/2}} = \left(\frac{N}{V}\right)\left(\frac{h^2}{2\pi m k T}\right)^{3/2}$$

$$2.6 \doteq \left(\frac{N}{V}\right)\left(\frac{h^2}{2\pi m k T}\right)^{3/2}$$

For a given $\frac{N}{V}$ this relation fixes a minimum value of T.

For temperatures lower than this the particles "condense" into the lowest state. In this case, it is incorrect to let $\Sigma \to S$ and our statistics no longer apply.

The fact that the molecules in a BE gas condense into the lowest state gives rise to an interesting state of affairs: If the molecules are all in the lowest state, we know their momentum extremely well and hence they can not be localized or contained. A possible test of this could be made by condensing

He_4 II and He_3 II

He_4 II obeys BE statistics and should condense. He_3 II obeys Fermi statistics and should not. Condensed He_4 II has no viscosity and flows uphill.

Important unsolved degeneracy problems are:

1) Liquid drop nucleus model
2) Superconductivity
3) He_4 II

Problem: Mayer 486 16.5
Repeat the above treatment for a 2 dimensional BE gas.

Gas with Structure

Classical Case

$$Z = \frac{1}{n!}\left(\sum_i e^{-E_i/kT}\right)^n$$

$$E_i = E^{CG} + E^{IN} + \underbrace{E^{\text{INTERACTION WITH NEIGHBOR}}}_{\text{neglect}}$$

$$Z = \frac{1}{n!}\left(\sum_i e^{-\frac{(E^{CG}+E^{IN})_i}{kT}}\right)^n$$

$$= \frac{1}{n!}\left(\sum_\alpha \sum_i e^{-\frac{E_\alpha^{CG}}{kT}} \cdot e^{\frac{E_i^{IN}}{kT}}\right)^n$$

$$\ln Z = -\ln n! + n \ln \sum e^{-E_{CG}/kT} + n \ln \sum e^{-E_{IN}/kT}$$

$$\ln Z = \ln Z^{\text{monatomic}} + \ln Z^{\text{internal}}$$

(We are dealing only with pure gases)

$$\sum e^{-E_i/kT} \equiv \sum_i g_i e^{-E_i/kT}$$

$g_i \equiv$ statistical weight of a single state.

Dec 2

$$\bar{E} = -\frac{\partial \ln Z}{\partial (\frac{1}{kT})}$$

$$\bar{E} = \frac{3}{2} NkT + N \frac{\sum_i g_i e^{-E_i/kT} E_i}{\sum_i g_i e^{-E_i/kT}}$$

Suppose that for a given application of the above formula the ground state energy is E_0. We can

rewrite it as follows:

$$\bar{E} = \frac{3}{2}NkT + N\frac{\sum_0^M g_i (E_i - E_0) e^{-(E_i - E_0)/kT}}{\sum_0^M g_i e^{-(E_i - E_0)/kT}} + NE_0$$

At "low" temperature

$$(E_1 - E_0) \gg kT$$

$$\bar{E} \to \frac{3}{2}NkT + NE_0$$

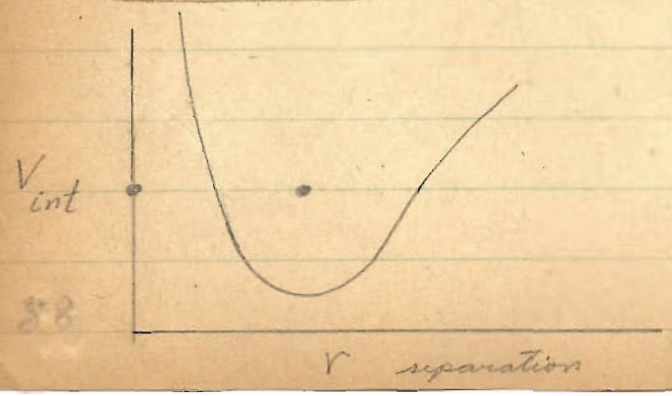
At "high" temperature

$$(E_i - E_0) \ll kT$$

$$\bar{E} \to \frac{3}{2}NkT + N\frac{\sum g_i (E_i - E_0)}{\sum g_i} + NE_0$$

Let us now take some models

Diatomic Gas



We shall first treat the dumbbell model. In the vibrational states the distance of the two atoms is fixed.

$$E_{vib} = (n + \tfrac{1}{2}) h\nu_0$$

The rotational states are:

$$E_{rot} = \frac{J(J+1)\hbar^2}{2I}$$

The statistical weight of the rotational states is

$$g_j = 2J + 1$$

The energy of the molecule is

$$E_i = E_0 + (n + \tfrac{1}{2}) h\nu_0 + \frac{J(J+1)\hbar^2}{2I}$$

Since the moment of inertia depends on the amplitude of the vibrations there should be an interference term. We neglect it.

Pure Oibrator

Problem: Prayer 6.3

Pure Rotator

$$E/kT = \frac{(J+1)J\hbar^2}{2IkT} = J(J+1)\sigma$$

where $\sigma = \frac{\hbar^2}{2IkT}$

$$Z_{rot} = \sum_0^\infty (2J+1)e^{-J(J+1)\sigma}$$

The following formula will be useful: Euler Maclauren Sum

$$\sum_{n=a}^{\infty} f(n) = \int_a^\infty f(x)dx + \frac{1}{2}f(a) - \frac{1}{12}f'(a) + \frac{1}{720}f''(a) + \frac{1}{30200}f'''(a) + \ldots$$

Dec. 4

Applying the EM formula to our sum:

$$\sum_0^\infty (2J+1)e^{-J(J+1)\sigma} = \int_0^\infty e^{-J(J+1)\sigma} d(J^2+J) + \ldots$$

$$= \frac{1}{\sigma} + \frac{1}{3}\left(-2\sigma\right)$$

If $\sigma << 1$ this formula is good.
If σ large we can sum:

$$\sum_0^\infty = 1 + 3e^{-2\sigma} + 5e^{-6\sigma} + \ldots$$

If necessary numerical methods may be used to get values in between the above limits.

Classical Limit $\sigma << 1$

$$(Z_{rot})^n \doteq \left(\frac{1}{\sigma}\right)^n$$

$$\bar{E} = -\frac{\partial \ln Z}{\partial\left(\frac{1}{kT}\right)} = +\frac{\partial}{\partial \frac{1}{kT}} n \ln \sigma$$

$$= n\,\frac{1}{\sigma}\,\frac{\hbar^2}{2I} = nkT$$

$$= 2\left\{\tfrac{1}{2} nkT\right\}$$

We approach the classical limit in case: $\frac{\hbar^2}{2IkT} \ll 1$

This means either

$\hbar \to 0$

I large

T large

In practice the only cases in which the rotational energy of a molecule is important is if the molecule contains H as P. Observations on band spectra indicate that this theory works very well (if correctly interpreted)

Specific Heat of H_2

According to our theory:

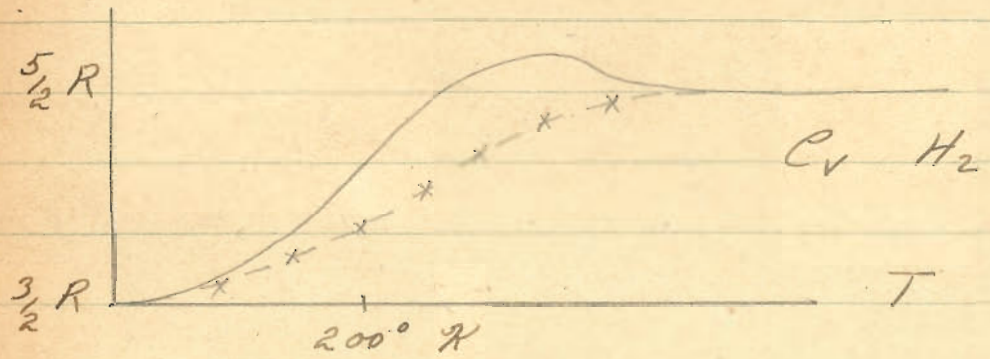
$$C_v^{H_2} = \frac{3}{2}R + \frac{2}{2}R$$

at high temps. and

$$C_v^{H_2} = \frac{3}{2}R$$

at low temps.

This much is O.K. In the transition region, the curve should look as solid curve below. This does not agree with the dotted experimental curve.



At first, people thought this was an effect of spin. An H nucleus has spin 1/2. Hence the total wave function must be antisymmetric with respect to interchange of the two nuclei. The spatial wave function is

sym. for L even
antisym for L odd

∴ the spin wave function must

Be:

sym for J odd ortho H ↑↑
antisym for J even para H ↑↓

For spin 1 Statis W. 3 ↑↑
" 0 " " 1 ↑↓

If we include the effect of spin, the total statistical weight for a state becomes

$$g_i = (2S+1)(2J+1)$$

and

$$Z_{rot} = 3 \sum_{1,3,5,\ldots} (2J+1) e^{-J(J+1)\sigma} + 1 \sum_{0,2,4,\ldots} (2J+1) e^{-J(J+1)\sigma}$$

It turns out that this Z does not give the correct C_v either. The reason for this is that it takes a very long time for equilibrium to be established between ortho and

para H (10 months in ichan glass ware). This is because there are no forces which intract strongly enough with the spins to turn them around.

At room temp, $\sigma << 1$

$$Z_{rot} = 3\bar{\sigma} + 1\cdot\bar{\sigma}$$

The ratio of ortho to para H is 3:1.

At low temp, $\sigma >> 1$

$$Z_{rot} \to 1\cdot 1 + 3\cdot 3e^{-2\sigma}$$

All the H is para H. Para H may be obtained by freezing and waiting for equilibrium. Equilibrium between para and ortho H may be hastened by the addition of a para magnetic gas or by adsorbing on charcoal.

The specific heat measured by early experimenters was the non-equilibrium value. We can get the correct specific

heat for this case by treating the gas as a mixture of two gases.

$$\bar{E} = \frac{3}{4}\bar{E}_{J\,odd} + \frac{1}{4}\bar{E}_{J\,even}$$

$$Z_{non\,eq} = \left(\sum_{J\,odd}(2J+1)e^{-J(J+1)\sigma}\right)^{\frac{3}{4}}\left(\sum_{J\,even}(2J+1)e^{-J(J+1)\sigma}\right)^{\frac{1}{4}}$$

$$= Z_o^{\frac{3}{4}} Z_e^{\frac{1}{4}}$$

This is to be contrasted to the equilibrium expression:

$$Z_{eq} = 3Z_{odd} + 1Z_{even}$$

Statistical Mechanics is good in the two extremes of complete equilibrium and no interaction

The molecule H-D can obviously be treated independently of the spin since the two particles are not identical.

Problem: Discuss the case of a $\bar{D} - \bar{D}$ molecule: statistics and partition function.

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Entropy and the Third Law

{ The first two laws of thermodynamics are expressible in the form

1) $\delta E = 0$

2) $\delta S \geq 0$ }

By definition:

$$S = -k \sum p_n \ln p_n$$

$$= +k \sum p_n \ln \frac{1}{p_n}$$

Where p_n is the probability the system is in the state n. Since $0 \leq p_n \leq 1$, the entropy is positive definite.

If at absolute zero there is one unique state, $p_n = 1$ and $S \to 0$

$$S = \frac{\partial}{\partial T}(kT \ln Z) = k \ln Z + \frac{\bar{E}}{T}$$

$$Z = \sum_{sys} e^{-E_i/kT}$$

$$= e^{-\frac{E_0}{kT}} \sum_{sys} e^{-(E_i - E_0)/kT}$$

$$\ln Z = -\frac{E_0}{kT} + \ln \sum e^{-(E_i - E_0)/kT}$$

$$S = k \ln \sum e^{-(E_i - E_0)/kT} + \frac{\bar{E} - E_0}{kT}$$

With one unique ground state:
i.e. $kT \ll$ any $(E_i - E_0)$

$$S = k \ln (1 + e^{-(E_i - E_0)/kT} + \ldots) + (\bar{E} - E_0)/kT$$

If the system is in the ground state $(\bar{E} - E_0)/kT = 0$. Also $T \to 0$, $S \to k \ln 1 = 0$

If the ground state is degenerate:

$$S \to k \ln g_0$$

where g_0 is the degeneracy of the ground state.

Important cases of degeneracy

1) Isotopes: If one fuzes a mixture of isotopes there will in general be degenerate states due to the small energy differences between different configurations

2) Ortho - Para case; allotropic forms of molecules.

3) Random Crystalization: An example of this is CO.

a) C≡O O≡C C≡O

b) C≡O C≡O C≡O

In fast fuzing, one does not get the lowest state of the crystal. g_0 for this case $= 2^N$

$S_{T=0} = N k \ln 2$

$= R \ln 2 = 1.4$ cal/mole degree

This effect has been measured.

4) Real Degeneracy: Atomic or Nuclear reactions. Spins can be assigned on the basis of entropy measurements.

Perfect Gas

We derived the partition function for a perfect gas assuming there was no degeneracy. Q.M. tells us that for low temperature there must be degeneracy since the wavelength of the particles becomes longer and longer with lower temperature and eventually it becomes impossible to distinguish between them. This means that at low temperatures we must use the proper Statistics.

In the classical case:

$$S_{MB} \to -\infty \quad \text{as} \quad T \to 0$$

This is N.G.

If the gas obeys Bose statistics

$$S_{BE} = k \ln Z_{BE} + \frac{E - E_0}{T}$$

As $T \to 0$

$$S_{BE} \to kN \ln 1 + 0 = 0$$

If the gas has spin

$$S_{BE} \to kN \ln(2S+1)$$

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For a Fermi Dirac gas there is a unique lowest state.

$$Z_{FD} = \prod_j \left(1 + e^{(E_0 - E_j)/kT}\right)$$

$$\ln Z_{FD} = \sum_j \ln\left(1 + e^{(E_0 - E_j)/kT}\right)$$

$$S_{FD} = \frac{\partial}{\partial T}(kT \ln Z_{FD})$$

$$= \frac{\partial}{\partial T} \sum kT \ln\left(1 + e^{(E_0 - E_j)/kT}\right)$$

$$S_{FD} = \frac{\partial}{\partial T}\left\{ \sum_{E_j < E_0} kT \cdot \frac{(E_0 - E_j)}{kT} + \sum_{E_j > E_0} kT \ln(1+\epsilon) \right\}$$

$$\to 0 \quad \text{as} \quad T \to 0$$

Isotope Mixtures
Perfect Gas

$$Z = \sum_{n\,m} \frac{n_1! n_2! \ldots m_1! m_2!}{N!\, M!} e^{\sum_n \frac{\epsilon}{kT} + \sum_m \frac{\epsilon}{kT}}$$

$$= \frac{1}{N!}\left(\sum_{\text{states}} e^{-\frac{\epsilon}{kT}}\right)^N \frac{1}{M!}\left(\sum_{\text{states}} e^{-\frac{\epsilon}{kT}}\right)^M$$

$$Z(n+m\ VT) = Z(n\ VT)\, Z(m\ VT)$$

$$\ln Z_{n\,m} = \ln Z_n + \ln Z_m$$

This means that all thermodynamic properties will be additive.

For a slightly degenerate monatomic perfect gas:

$$Z_n = \frac{1}{n!}\left[\frac{(2\pi m k T)^{3/2} V g_0}{h^3}\right]^n$$

where g_0 is the degeneracy of a single particle.

For $n \gg 1$ this partition function should give thermodynamic results.

$$\ln n! \sim \tfrac{1}{2}\ln 2\pi n + n(\ln n - 1)$$

$$\ln Z = n\left[\ln(2\pi m k T)^{3/2} + \ln V - \ln n + 1 + \ln g_0/h^3 - \tfrac{1}{2n}\ln 2\pi n\right]$$

For large n, the last item may be neglected.

Suppose we mix two gases at constant pressure. The mole fraction of one of the gases is $x_1 = V_1/V$ where V is the volume of the two gases at pressure P and V_1 is the volume of the one gas at P.

$$\ln Z(n_1 + n_2, P, T) = \ln Z(n_1, P, T)$$

$$+ \ln Z(n_2, P, T) + n_1 \ln V - n_1 \ln V_1$$
$$+ n_2 \ln V - n_2 \ln V_2$$

$$= \ln Z(n_1, P, T) + \ln Z(n_2, P, T)$$
$$- n_1 \ln X_1 - n_2 \ln X_2$$

Hence even tho we are dealing with two gases which are identical except for the tags they carry there is an entropy change involved when they are mixed. The other thermodynamic functions all involve derivatives of $\ln Z$ and are unchanged.

Problem: Calculate the minimum entropy required to separate 1 kg U^{235}. What is the energy required at 300° K

$$X_{235} = 1/140$$
$$X_{238} = 139/140$$

How much energy is required if the separation is carried out by ionizing each atom ~ 10 V/atom

Mixed Crystal

1) No volume change
2) All interactions identical

$$Z_{AB} = Z_{AB}(E_0\ T\ \Theta)\ G_{AB}$$

Θ = Debye temperature

$$Z_A = Z_A(E_0\ T\ \Theta)\ G_A$$
$$Z_B = Z_B(E_0\ T\ \Theta)\ G_B$$

$$\ln Z_{AB} = \ln Z_A + \ln Z_B + \ln \frac{G_{AB}}{G_A G_B}$$

$$G_{AB} = \frac{(n_A + n_B)!}{n_A!\, n_B!}\ G_A\ G_B$$

$$\ln Z_{AB} = \ln Z_A + \ln Z_B + \ln \frac{(n_A + n_B)!}{n_A!\, n_B!}$$

$$= \ln Z_A + \ln Z_B$$

$$- n_A \ln X_A - n_B \ln X_B$$

The above equation defines a "perfect" mixture: Only the entropy is changed.

General Condition for Equilibrium

$$\delta F = 0$$

$$F = \sum_i (E + pV - TS)_i$$

Ref Zemansky or Epstein

The above condition implies that the temperature and pressure of all phases of the system is the same.

Transfer:

$$\sum_i \left(\frac{\partial F}{\partial n_i}\right)_{pT n_j} \delta n_i = 0$$

$$\sum_i \mu_i \, \delta n_i = 0$$

$\mu_i = \left(\frac{\partial F}{\partial n_i}\right)_{pT n_j}$ = partial molal

thermodynamic potential. A restriction is imposed on the δn_i.

$$\sum \nu_i G_i = 0$$

ie $1(H_2O) - 2(H) - 1(O) = 0$

We must have conservation in transfer

$$\delta n_1 : \delta n_2 : \delta n_3 \ldots = \nu_1 : \nu_2 : \nu_3 \ldots$$

$$\delta n_i = \nu_i \delta K_0$$

$$\sum_i \mu_i \nu_i \delta K_0 = 0$$

δK_0 arbitrary

$$\therefore \sum \mu_i \nu_i = 0$$

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Equilibrium of a vapor above its solid.

$$A_{gas} \rightleftarrows A_{solid}$$

$$\sum \nu_i \mu_i = \mu_g - \mu_s = 0$$

If F additive

$$F(n) = n F(1)$$

$$F_g = F_s$$

$$F = E + pV - TS$$

Assume no degeneracy - monatomic gas.

$$F = E + pV - T\left(n\frac{\epsilon - \epsilon_0}{T} + nk\ln\left(2\pi m k T\right)^{3/2}\frac{V}{h^3} + nk\ln e^{n} + nk\ln\sum_{elec}\frac{g_i}{g_0}e^{-(\epsilon-\epsilon_0)/kT} + nk\ln g_0\right)$$

$$F_g = n\epsilon_0 + nkT\ln p - \frac{5}{2}nkT\ln T - nkT\ln\sum_{elec}\frac{g_i}{g_0}e^{-(\epsilon_i-\epsilon_0)/kT}$$

$$-nkT\ln(2\pi m)^{3/2}k^{5/2}\frac{g_0}{h^3} + pV - nkT\ln e.$$

where we have used the relation

$$pV = nkT$$

$$F_s = E - TS$$

For the solid state which is very dense we neglect the term pV. We shall also assume that the temperature $\ll$ any $(\epsilon - \epsilon_0)$ i.e. the solid is in its "ground" state

$$F_s = E_0 - T k \ln G_0$$

$$G_0 = g_{0s}^{\,n}$$

$$= n\epsilon_{0s} - nkT \ln g_{0s}$$

We can get the vapor pressure by equating $F_g = F_s$ and solving for $\ln p$

$$\ln p = \frac{\epsilon_{0s} - \epsilon_0}{kT} + \frac{5}{2}\ln T - \ln \sum \frac{g_i}{g_0} e^{-(\epsilon - \epsilon_0)/kT}$$

$$+ \ln \frac{(2\pi m)^{3/2} k^{5/2} g_0}{h^3 g_{0s}}$$

This equation gives an absolute value for the pressure in terms of physical constants, the temperature and the latent heat per molecule, $(\epsilon_{0s} - \epsilon_0)$. The expression is best at low temperatures.

Thermodynamic considerations give the pressure within an additive constant only.

$$\frac{d}{dT}(\ln p) = \frac{L(T)}{RT^2}$$

Integrate (Ref Zemansky p 293)

$$\ln p = -\frac{L(0)}{RT} + \frac{5}{2}\ln T + \int_0^T \left\{ \int_0^{T_1} \frac{1}{R T_1^2} \Delta_{G-S} C_p \, dT \right\} dT_1$$

$$+ \text{const.}$$

If we have the same mixture of isotopes in the vapor as in the solid, we can treat each isotope individually so there is no question of entropy change in going from the solid to vapor phase.

The statistical theory gives good agreement with experiment. The theory also fits H_2 at temperatures sufficiently low so that rotational states are not excited. Test have been made on:

	g_{os}	g_o
Hg, Cd, Zn, Pb, A	1	1
H_2	1	1
Na	1	2

Na has spin $\frac{1}{2}$. As a gas it is degenerate. In the solid state however, the electron

gas goes into the lowest F D state and the system is non-degenerate.

Problem: Calc the vapor pressure of D_2 H_2 HD at 25° K.

Diatomic Molecule

$$F_g = n\epsilon_0 + nkT\ln p - \frac{5}{2}nkT\ln T$$

$$-nkT\ln(2\pi m)^{3/2}k^{5/2}\frac{g_0}{h^3} - nkT\ln\sum_{\substack{vib\\ J\\ elec}}\frac{(2J+1)}{g_0}g_{ve}e^{-\frac{(\epsilon-\epsilon_0)}{kT}}$$

The last term may be broken up as follows:

$$-nkT\ln\sum_{J_0}(2J+1)e^{\frac{J(J+1)h^2}{2IkT}} - nkT\ln\sum_{v\text{-}e}\frac{g_{ve}}{g_0}e^{-(\epsilon_{ve}-\epsilon_0)/kT}$$

$$= -nkT\ln\frac{2IkT}{h^2\sigma} - nkT\ln\sum_{ve}\frac{g_{ve}}{g_0}e^{-(\epsilon_{ve}-\epsilon_0)/kT}$$

where σ is the symmetry

number $\sigma = 1$ for AB

$= 2$ for AA

We can now handle the reaction:

$$A_2 + B_2 \rightleftarrows 2AB$$

If we proceed in a way we have done for a monatomic gas we can get an expression for

$$\ln \frac{P_{A_2} P_{B_2}}{(P_{AB})^2} = \ldots$$

Our final expression for F_g diatomic is:

$$F_g = n\epsilon_0 + nkT \ln p - \frac{7}{2} nkT \ln T$$

$$- nkT \ln \sum_{v\ell} \frac{g_{v\ell}}{g_0} e^{-(\epsilon_{v\ell} - \epsilon_0)/kT}$$

$$- nkT \ln \frac{2Ik}{\hbar\sigma} - nkT \ln (2\pi m)^{3/2} k^{5/2} \frac{g_{i0}}{h^3}$$

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Some Properties of Radiation

$$\ln Z_{rad} = -\sum_i \left\{ \ln\left(1 - e^{-\frac{h\nu_i}{kT}}\right) + \frac{h\nu_i}{2kT} \right\}$$

In empty space $\sum \to \int P(\nu)\,d\nu$

$$P(\nu)\,d\nu = 2 \cdot \frac{4\pi p^2 dp V}{h^3} = \frac{8\pi V \nu^2 d\nu}{c^3}$$

$$\bar{E} = kT^2 \frac{\partial \ln Z}{\partial T}$$

$$= \sum_i \left\{ \frac{h\nu_i}{\left(e^{h\nu_i/kT} - 1\right)} + \frac{h\nu_i}{2} \right\}$$

$$S = \frac{\bar{E}}{T} + k \ln Z$$

$$S = \sum_i \left\{ \frac{h\nu_i}{T\left(e^{h\nu_i/kT} - 1\right)} + \frac{h\nu_i}{2T} \right\}$$

$$+ k \left[- \sum_j \left\{ \ln\left(1 - e^{-h\nu_j/kT}\right) + \frac{h\nu_j}{kT} \right\} \right]$$

Let us evaluate $\sum_j \ln\left(1 - e^{-h\nu_j/kT}\right)$ explicitely explicitely

$\ln Z_{rad} \rightarrow \ln \bar{E} \rightarrow$

$$\frac{8\pi V}{c^3}\int_0^\infty \nu^2 d\nu \ln\left(1-e^{-\frac{h\nu}{kT}}\right)$$

$$-\ln(1-x) = x + \frac{x^2}{2} + \frac{x^3}{3} + \dots \qquad |x|<1$$

$$= -\int_0^\infty \nu^2 d\nu \left(e^{-h\nu/kT} + \frac{1}{2}e^{-2h\nu/kT} + \dots\right)$$

$$= -\left(\frac{kT}{h}\right)^3 \sum_1^\infty \frac{1}{n^4}\int_0^\infty e^{-y} y^2 dy$$

$$= -\left(\frac{kT}{h}\right)^3 2\sum_1^\infty \frac{1}{n^4}$$

$$= -2\left(\frac{kT}{h}\right)^3 \frac{\pi^4}{90}$$

$$\ln Z = \frac{8\pi V}{45}\left(\frac{kT}{hc}\right)^3 - \sum_j \frac{h\nu_j}{2kT}$$

$$\bar{E} = \left(\frac{k^4}{h^3c^3}\frac{8}{15}\pi^5\right)VT^4 + \sum_j \frac{h\nu_j}{2}$$

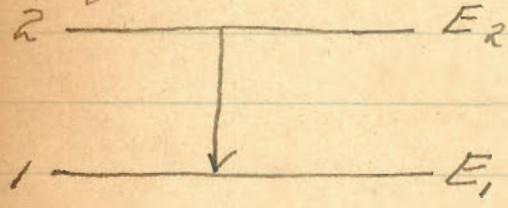
$$S = \frac{8\pi^5 V k^4 T^3}{45 c^3 h^3} + \frac{3k^4T^3 8\pi^5 V}{45 c^3 h^3}$$

$$= \left(\frac{k^4}{h^3c^3}\frac{32}{45}\pi^5\right)VT^3$$

$$P_R = \frac{\partial \ln Z}{\partial V} = kT \frac{8\pi^5}{45 h^3 c^3} (kT)^3$$

$$= \frac{1}{3} \bar{E}/V$$

Third Derivation of Planck's Law
Einstein A & B coefficients.
Assume a set of atoms in equilibrium with radiation.
Consider two states of the system.



$$h\nu = E_2 - E_1$$

The transition prob / sec

$2 \to 1$

A_{21} spontaneous emission.
$B_{21}\,u(\nu)$ induced emission

$1 \to 2$

$B_{12}\,u(\nu)$ absorption

where $u(\nu)$ = density of radiation at ν.

If we assume <u>detailed balance</u>, then at equilibrium we have:

$$2 \to 1 \quad = \quad 1 \to 2$$

$$N_2 (A_{21} + B_{21} u(\nu)) = N_1 B_{12} u(\nu)$$

$$\frac{N_2}{N_1} = e^{-(E_2 - E_1)/kT} = e^{-h\nu/kT}$$

i.e. Maxwell distribution

$$u(\nu)\left[-B_{21} e^{-h\nu/kT} + B_{12} \right] = A_{21} e^{-h\nu/kT}$$

$$u(\nu) = A_{21} / \left[B_{21} e^{h\nu/kT} - B_{21} \right]$$

$B_{21} = B_{12}$ Since B Hermitian

$$u(\nu) = \left(\frac{A_{21}}{B_{12}}\right) \frac{1}{(e^{h\nu/kT} - 1)}$$

To find $\frac{A_{21}}{B_{12}}$, go to the classical limit, Rayleigh Jeans Law

$$u(\nu) = \frac{8\pi\nu^2}{c^2} 2 \cdot \frac{kT}{2}$$

$$\frac{A_{21}}{B_{12}} = \frac{8\pi h\nu^3}{c^3}$$

This implies a black body has spectral absorbtion lines at every frequency. A solid is not a bad black body a optical frequencies because of the density of states.

Problem: Show that the spontaneous emission is equiv to emission induced by one quantum per state of the field i.e. $A_\nu / B_\nu = 1$

1/6/48

Fluctuations:

The probability of finding a system in a state, i, is:

$$P(i) = e^{(\psi - E_i)/kT}$$

Let x represent the value of some macroscopic variable which belongs to the system. Our

object is to calculate the fluctuation about x of this variable.

The probability of x is:

$$P(x) = C \sum_{n(x)} e^{-E_n/kT}$$

where the sum is taken over those states of the system compatible with x.

$$= K Z(x)$$

$$= K' e^{-A(x)/kT}$$

$A(x) = -kT \ln Z(x)$ = Helmholtz free energy.

We can write

$$P(x) = P(x_0) e^{-(A(x) - A(x_0))/kT}$$

where x_0 is the equilibrium value of the variable considered. If the fluctuations in x are not

too large, we can assume that the differential of the probability of finding the system in a state compatible with x is equal to the probability density times the differential of x.

$$dP(x) \equiv \omega(x)\,dx = \left.\frac{\partial P}{\partial x}\right|_{x_0} dx$$

By definition

$$\overline{(x-x_0)^2} = \frac{\int_0^\infty (x-x_0)^2\,\omega(x)\,dx}{\int_0^\infty \omega(x)\,dx}$$

Expand $A(x) - A(x_0)$ in a Taylor Series about x_0

$$A(x) - A(x_0) = \left.\frac{\partial A}{\partial x}\right|_{x_0}(x-x_0) + \left.\frac{\partial^2 A}{\partial x^2}\right|_{x_0}\frac{(x-x_0)^2}{2} + \cdots$$

$\left.\frac{\partial A}{\partial x}\right|_{x_0} = 0$ since x_0 is assumed to be the equilibrium position.

$$P(x) \doteq P(x_0)\, e^{-\left.\frac{\partial^2 A}{\partial x^2}\right|_{x_0}\frac{(x-x_0)^2}{2kT}}$$

$$\omega(x) = P(x_0)\left(-\frac{\partial^2 A}{\partial x^2}\Big/\frac{2(x-x_0)}{2kT}\right) e^{-\frac{\partial^2 A}{\partial x^2}\Big/_{x_0}\frac{(x-x_0)^2}{2kT}}$$

$$\overline{(x-x_0)^2} = \frac{\int_{-\infty}^{\infty}(x-x_0)^2 e^{-\frac{\partial^2 A}{\partial x^2}\Big/_{x_0}\frac{(x-x_0)^2}{2kT}} d(x-x_0)^2}{\int_{-\infty}^{\infty} e^{-\frac{\partial^2 A}{\partial x^2}\Big/_{x_0}\frac{(x-x_0)^2}{2kT}} d(x-x_0)^2}$$

$$\overline{(x-x_0)^2} = kT \Big/ \frac{\partial^2 A}{\partial x^2}\Big/_{x_0}$$

The extension to $+\infty$ and $-\infty$ is justified if most of the contribution to the integral comes from values near x_0. This will be the case if $\partial^2 A/\partial x^2 / 2kT$ is large, i.e. $\overline{(x-x_0)^2}$ small. This formula is valid only if $\partial^2 A/\partial x^2$ is positive. This implies that A has a minimum which in turn implies a stable equilibrium.

$$\overline{(A-A_0)} = \frac{\partial^2 A}{\partial x^2}\Big/_{x_0}\frac{\overline{(x-x_0)^2}}{2} = kT/2$$

Classically we have

$\Delta A = \frac{1}{2}kT \times$ no. degrees of freedom.

Density Fluctuations of a perfect gas.

$$p = -\left.\frac{\partial A}{\partial V}\right|_T$$

$$\overline{\Delta V^2} = kT \Big/ -\left.\frac{\partial P}{\partial V}\right|_{TN} = kT \Big/ NkT/V^2$$

$$\overline{\Delta V^2} = \frac{V^2}{N}$$

$$\sqrt{\frac{\overline{\Delta V^2}}{V^2}} = \frac{1}{\sqrt{N}}$$

Real Gas

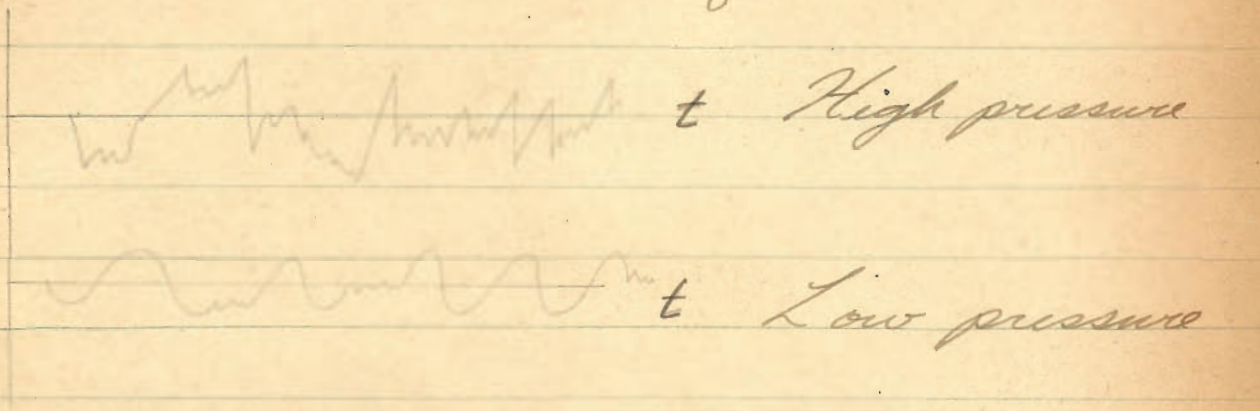


At the critical point for a real gas $\frac{\partial p}{\partial V} = \frac{\partial^2 p}{\partial V^2} = 0$

This means large V (infinite) fluctuations in density. These large fluctuations give rise to large scattering of light. "Opalescence" is actually observed in gases near the critical point.

Fluctuations in measuring instruments.

Brownian motion of a mirror.



The energy associated with this motion is $\frac{1}{2} kT$.

As a consequence of equipartition we have uniform power in every frequency interval. It cut off occurs at $h\nu \sim kT$. For freq. above this the Planck distribution must be used.

Measuring Instrument

x = quantity to be measured

q = response of instrument

For most instruments the energy associated with the response of the instrument is:

$$\Delta W_q^S = A \frac{(\delta q)^2}{2}$$

The energy associated with instrument noise is:

$$\overline{\Delta W_q^N} = \frac{kT}{2}$$

A lower limit of measurable deflections occurs about at

$$\overline{\Delta W_q^N} = \overline{\Delta W_T^S}$$

$$\langle \delta q \rangle = \sqrt{kT/A}$$

$$F_q = \frac{\partial W}{\partial (\delta q)} = A \delta q$$

$$F_x = B \delta x$$

At equilibrium $F_x = F_q$

$$A \delta q = B \delta x$$

$$\langle \delta x \rangle = \frac{A}{B} \langle \delta q \rangle$$

$$\langle \delta x \rangle = \sqrt{kTA}/B$$

Examples:

I Chemical Balance

$$lg\,\delta m = B\,\delta m$$

$$I\ddot{\delta\theta} = -A\delta\theta$$

$$\tau = 2\pi\sqrt{I/A}$$

$$A = (2\pi)^2 I/\tau^2$$

$$\langle \delta m \rangle = \frac{2\pi\sqrt{I}}{\tau lg}\sqrt{kT}$$

II Spring Balance

$\delta q = \delta z =$ spring elongation

$$F_z = K\,\delta z = A\delta z$$

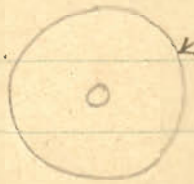
$$F_m = g\,\delta m = B\delta$$

$$\langle \delta m \rangle = \sqrt{kTK}/g$$

$$\left(\frac{2\pi}{\tau}\right)^2 = \frac{K}{M} \quad \therefore \sqrt{K} = \frac{2\pi}{\tau}\sqrt{M}$$

$$\langle \delta m \rangle = \frac{2\pi}{\tau g}\sqrt{M}\sqrt{kT}$$

III Bolometer



$$(T - T_B) = \theta$$

In this case the response we measure is θ. In order to find the fluctuations in the temperature we must modify our formula

$$\overline{(X - X_0)^2} = \frac{\partial^2 A}{\partial X^2}\Big|_{X_0} kT$$

In deriving this formula we expanded A which appeared in the exponential $e^{-\frac{A}{kT}}$ in a Taylor Series. In this case we must expand the whole exponent

$$\frac{A}{kT} = \frac{E}{kT} - \frac{S}{k}$$

We obtain:

$$\overline{\theta^2} = k \Big/ \frac{\partial^2}{\partial T^2}\left(\frac{E}{T} - S\right)\Big/_{T_B}$$

$$E = CT$$

$$S = C\int_0^T \frac{dT}{T} + S_0$$

$$\frac{\partial^2\left(\frac{E}{T}\right)}{\partial T^2} \quad \frac{\partial^2 S}{\partial T^2} = 0$$

$$\frac{\partial^2 S}{\partial T^2} = -\frac{C}{T^2}$$

$$\overline{\theta^2} = kT^2/C$$

Cooling rate $C\frac{d\theta}{dt} = -K\theta + H(T)$

Newtons Law of cooling

$H(T)$ = absorbed energy

H_s = incident energy

$\epsilon H_s = H$

$$\overline{H_s^2} = \frac{\overline{H^2}}{\epsilon^2} \text{ by eq. } \frac{K^2\overline{\theta^2}}{\epsilon^2} = \frac{K^2}{\epsilon^2}\frac{kT^2}{C}$$

$$\tau = \frac{C}{K} = \text{time constant}$$

$$\overline{H_0^2} = \frac{KkT^2}{\epsilon\tau} = \frac{CkT^2}{\tau^2}$$

$$\langle H_s \rangle = \sqrt{kT}\,\frac{\sqrt{CT}}{\epsilon T}$$

For radiation $K = K(T) \sim T^3$

Johnson Noise



1) Independent of resistor material.
2) Same frequency spectrum

Power $= f(R\,T\,\nu)$

$E^2(\nu)\,d\nu = 4RkT\,d\nu$

Ref: Bell Telephone 1934 - Rice
A Nyquist. Phys Rev. 1928

Problem: What happens at high frequencies?

Jan 13

Free electron theory of metal

Assume electrons are in thermal equilibrium with the lattice.

If the electrons obeyed MB statistics, we should have a contribution to the specific heat of $\frac{3}{2}kT$ per electron.

For a metal having a single valence electron this would amount to $\frac{3}{2}R$ per mole. This is in serious disagreement with experiment which finds that the specific heat of all solids, metals and non metals, is about $3R$ at room temperature. Any contribution of the electrons must be small.

Let us investigate what happens if we use FD statistics for the electrons.

$$\bar{n}_i = \frac{1}{(e^{(E_i - E_0)/kT} + 1)}$$

$$p^2 = 2mE$$

$$\frac{dp}{dE} = \frac{m}{p}$$

$$n(E)dE = V \cdot \frac{4\pi p^2}{h^3} \frac{m}{p} dE \cdot \frac{2}{(e^{(E_i - E_0)/kT} + 1)}$$

$$= V \cdot \frac{8\pi \sqrt{2m}\, m}{h^3} \cdot \frac{E^{1/2} dE}{(\quad)}$$

In the case $kT \to 0$ we have shown

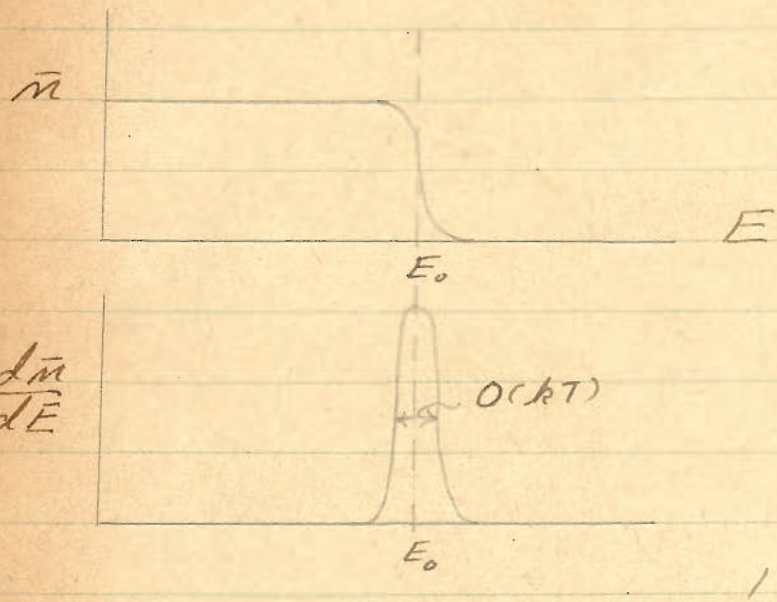
$$E_0(0) = \frac{h^2}{2m}\left(\frac{3\pi^2 N}{V}\right)^{2/3}$$

Typical values of E_0 are:

	val.	E_0
Li	1	4.7 ev.
Ca	2	4.2
Au	1	5.5
Al	3	11.7

At room temp $kT \sim \frac{1}{40}$ ev. These results are independent of temperature but quite good.

We wish to investigate the case $\frac{kT}{E_0} << 1$



Let $f(E) = \frac{1}{(e^{(E-E_0)/kT}+1)} = \bar{n}$

$$\bar{A} = \int_0^\infty A(E) f(E) dE$$

$$A(E) = \frac{d\phi}{dE}$$

$$\bar{A} = \int_0^\infty \phi' f(E) dE$$

$$= \phi f(E) \Big|_0^\infty - \int_0^\infty \phi \frac{df(E)}{dE} dE$$

$$= -\phi(0) \frac{1}{(e^{-E_0/kT}+1)} - \int_0^\infty \phi f(E) dE$$

In our approx $e^{-E_0/kT} \ll 1$

$$\bar{A} = -\phi(0) - \int_0^\infty \phi(E) f'(E)\, dE$$

Expand $\phi(E)$ about E_0

$$\phi(E) = \phi(E_0) + \phi'|_{E_0}(E-E_0) + \phi''|_{E_0}\frac{(E-E_0)^2}{2} + \dots$$

$$f'(E) = -\frac{e^{-(E-E_0)/kT}}{kT\left(e^{(E-E_0)/kT}+1\right)^2}$$

Let $x = \dfrac{E-E_0}{kT}$

$$\bar{A} = -\phi(0) + \int_{-\frac{E_0}{kT}}^\infty dx \frac{e^x}{(e^x+1)^2}\left(\phi(E_0) + kT x \phi'|_{E_0} + \dots\right)$$

$$= -\phi(0) + \phi(E_0) + 0 + \int_{-\infty}^\infty \frac{(kT)^2}{2}\phi''|_{E_0}\frac{x^2 e^x}{(e^x+1)^2}dx + 0 + \dots$$

$$\int_{-\infty}^\infty \frac{x^2 e^x\, dx}{(e^x+1)^2} = \int_{-\infty}^\infty \frac{x^2 e^{-x}\, dx}{(1+e^{-x})^2}$$

$$= 2\int_0^\infty dx\, x^2 e^{-x}(1 - 2e^{-x} + 3e^{-2x} - \dots)$$

$$= -2\sum_{m=1}^\infty \int_0^\infty dx\, x^2 e^{-mx}\, m(-1)^m$$

$$= -4\sum_1^\infty \frac{(-1)^m}{m^2} = \frac{4\pi^2}{12} = \frac{\pi^2}{3}$$

$$\bar{A} = -\phi(0) + \phi(E_0) + \frac{\pi^2}{6}(kT)^2 \phi''(E_0) + \ldots$$

$$= \int_0^{E_0} A(E)\,dE + \frac{\pi^2}{6}(kT)^2 A'(E_0) + \ldots$$

Let us compute $\bar{N}$

$$\bar{N} = \int n(E)\,dE = \int \frac{\sqrt{2}\,m^{3/2}}{\pi^2 \hbar^3} V \sqrt{E}\, f(E)\,dE$$

$$= \frac{\sqrt{2}\,V m^{3/2}}{\pi^2 \hbar^3} \int E^{1/2} f(E)\,dE$$

$$= C\left[\frac{2}{3} E_0^{3/2}(T) + \frac{\pi^2}{6}(kT)^2 \frac{1}{2} E_0^{-\frac{1}{2}}(T) + \ldots\right]$$

$$N = C\,\frac{2}{3} E_0^{3/2}(T)\left(1 + \frac{\pi^2}{8}\left(\frac{kT}{E_0}\right)^2 + \ldots\right)$$

$$E_0(T) \approx \left(\frac{3N}{2C}\right)^{2/3}\left(1 - \frac{\pi^2}{12}\left(\frac{kT}{E_0(0)}\right)^2\right)$$

Problem: In this approx find the number of electrons above $E_0(T)$.

Specific Heat

$$\bar{E} = \int_0^\infty E \underbrace{C\sqrt{E}\, f(E)}_{n(E)}\,dE$$

$$\bar{E} = C\left[\int_0^{E_0(T)} E^{3/2}\,dE + \frac{\pi^2}{6}(kT)^2\,\frac{3}{2}\,E_0^{1/2}(T) + \ldots\right]$$

$$C_{v_{elec}} = \frac{\partial \bar{E}}{\partial T} = C\left[E_0^{3/2}(T)\,\frac{\partial E}{\partial T} + \frac{\pi^2}{2}k^2T\,E_0^{1/2}(T) + \frac{\pi^2}{6}(kT)^2\,\frac{3}{2}\,\frac{1}{2}\,E_0^{-1/2}(T)\,\frac{\partial E}{\partial T} + \ldots\right]$$

Jan 16

$$E_0(T) = E_0\left[1 - \frac{\pi^2}{12}\left(\frac{kT}{E_0}\right)^2\right]$$

Substitute $E_0(T)$ into expression for $C_{v_{elec}}$ keeping only terms of first order in (kT/E_0)

$$C_{v_{elec}} = C\left[E_0^{3/2}(0)\left(-\frac{\pi^2}{6}\frac{k^2T}{E_0}\right) + \frac{\pi^2}{2}k^2T\,E_0^{1/2}(0) + \ldots\right]$$

$$= C\,E_0^{3/2}(0)\,\frac{kT}{E_0}\left[-\frac{\pi^2}{6} + \frac{\pi^2}{2}\right]$$

$$= \frac{3}{2}Nk\,\frac{kT}{E_0}\,\frac{\pi^2}{3}$$

$$C_{v_{elec/mol}} = \frac{\pi^2}{2}R\left(\frac{kT}{E_0}\right)$$

It is apparent from the values of $E_0(0)$ quoted above

that C_{elec} is a very small correction to the specific heat at room temperatures.

$$\frac{C_{elec}}{C_{class}} = \frac{1}{60}\,\frac{T}{T_{room}}$$

At low temperatures

$$C_{Debye} = \frac{12\pi^4}{5} R \left(\frac{T}{\theta}\right)^3$$

$$\frac{C_{elec}}{C_{Debye}} = \frac{5}{24\pi^2}\left(\frac{kT}{E_0}\right)\left(\frac{\theta}{T}\right)^3$$

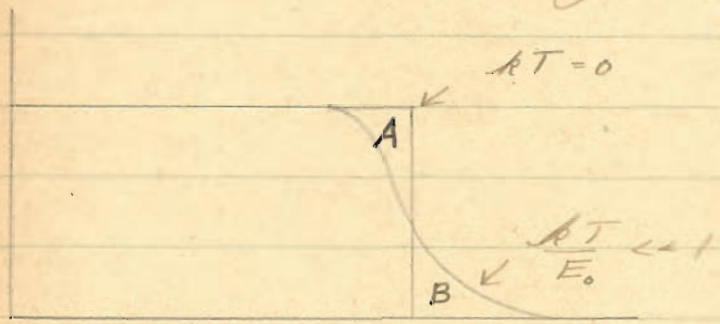
For $\theta \sim 100$ $\quad E_0 \sim 1\,ev$

$$\frac{C_{elec}}{C_{Debye}} \sim 1 \quad \text{at } 1^\circ K.$$

Agreement of this theory with experiment is discussed in Seitz. It is fair.

An order of magnitude result for C_{elec} may be obtained

in the following way.



Compute the change in the energy due to the electrons which have been displaced from A to B by the "small" temperature rise T.

$$\text{Area } B \sim kT \cdot 1$$

$$\frac{N}{E_0 \cdot 1} = \frac{n_{eff}}{kT \cdot 1}$$

$$n_{eff} = \frac{N}{E_0} kT$$

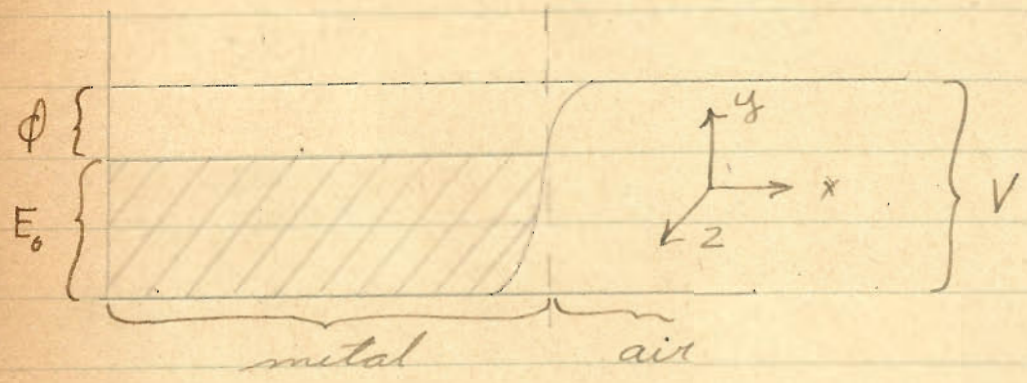
$$E = N\left(\frac{kT}{E_0}\right) kT$$

$$C_{v_{elec}} = \frac{\partial E}{\partial T} \sim Nk\frac{kT}{E_0}$$

$$\sim R\frac{kT}{E_0}$$

We have developed an equilibrium statistical theory. We can apply it to non-equilibrium problems to get approx results.

Thermionic Emission



Minimum Escape energy

$$E = E_0 + \phi + \frac{P_x^2 + P_y^2}{2m}$$

Classical calculation: FD statistics.

$$dj = e\, n(\bar{p})\, d\bar{p}\, V_x$$

$$dj = e\, n(p) \frac{\partial E}{\partial p_x} dp_x dp_y dp_z$$

$$j = e \int_{-\infty}^{\infty} dp_z \int_{-\infty}^{\infty} dp_y \int_{E_{esc}}^{\infty} dp_x\, n(p) \frac{\partial E}{\partial p_x}$$

$$n(p) = \frac{1}{(e^{(E-E_0)/kT} + 1)} \frac{2}{h^3}$$

$$j = \frac{2e}{h^3} \int_{-\infty}^{\infty} dp_z \int_{-\infty}^{\infty} dp_y \int_{E_{esc}}^{\infty} dE_x \frac{1}{e^{(E-E_0)/kT} + 1}$$

$$= \frac{2e}{h^3} \int_{-\infty}^{\infty} dp_z \int_{-\infty}^{\infty} dp_y \int_{E_{esc}}^{\infty} \frac{e^{-(E-E_0)/kT} dE}{(1 + e^{-(E-E_0)/kT})}$$

$$= \frac{2e}{h^3} \iint dp_z dp_y\, kT \ln\left(1 + e^{-(E_{esc} - E_0)/kT}\right)$$

$$= \frac{2e}{h^3} kT \iint dp_z dp_y\, e^{-\left[\phi + \frac{p_z^2 + p_y^2}{2m}\right]/kT}$$

$$= \frac{2e}{h^3} kT\, e^{-\phi/kT} \cdot (2mkT)\pi$$

$$= \frac{4\pi e m k^2}{h^3} T^2 e^{-\phi/kT}$$

$$= 120\, T^2 e^{-\phi/kT} \text{ amp/cm}^2$$

This theory is difficult to check. In general it is not to good. One has to worry about

surface irregularities, binding of electrons, variation of V_0 with temperature.

Problem: Find the classical current density. NB statistics.

Jan 20

Electro Magnetic properties of matter.

$\bar{m}$ } magnetic
$\bar{p}$ } electric } dipole moment per unit volume

$$\bar{m} = K \bar{H}$$
$$\bar{p} = \chi \bar{E}$$

Helmholtz Free Energy

$$A = A(T V \{^{H}_{E}\})$$
$$= U - TS + \bar{m} \cdot \bar{H}$$

$$m_z = - \frac{\partial A}{\partial H_z}$$

$$\chi = -\frac{1}{H_z}\frac{\partial A}{\partial H_z}$$

$$A = -kT \ln Z$$

$$Z = \sum e^{-E_i/kT}$$

Let us treat the case of a paramagnetic gas. In this case, the off-diagonal elements of the susceptibility tensor are zero so we can treat it as a vector. We shall associate with each molecule a dipole moment of fixed value. Our object is to compute the equilibrium value of the dipole moment per unit volume in the presence of a magnetic field H_z.

This model is not bad for O_2, NO, the alkali metals, crystal or dilute solutions of rare earth compounds.

$$Z = (\quad)\left(\sum_{M=-J}^{J} e^{-H_z M g_L \mu_B / kT}\right)^N$$

$M g_L \mu_B$ = magnetic moment in Z direction = $g_L \frac{e\hbar}{2mc} M$

Let:

$$\alpha = \frac{g_L \mu_B H_z}{kT}$$

$$\sum_{-J}^{J} e^{-\alpha M} = e^{-\alpha J}\left(1 + e^{\alpha} + e^{2\alpha} + \dots e^{2J\alpha}\right)$$

$$= e^{-\alpha J}\left(1 - e^{(2J+1)\alpha}\right)/\left(1 - e^{\alpha}\right)$$

$$= \sinh \alpha\left(J + \tfrac{1}{2}\right) / \sinh \alpha/2$$

$$\ln Z = N \ln\left(\frac{\sinh \alpha(J+\frac{1}{2})}{\sinh \alpha/2}\right)$$

$$K = \frac{NkT}{H_z}\frac{\partial}{\partial H_z} \ln(\quad)$$

$$= \frac{NkT}{H_z}\frac{g_L \mu_B}{kT}\frac{\partial}{\partial \alpha} \ln(\quad)$$

$$= \frac{N g_L \mu_B}{H_z} J\left[\frac{J+\frac{1}{2}}{J} \coth \alpha\left(J+\tfrac{1}{2}\right) - \frac{1}{2J} \coth \alpha/2\right]$$

Limiting cases $\alpha >> 1$

$$\frac{E_{mag}}{kT} >> 1$$

$$K = N g_L \mu_B \frac{J}{H_z}$$

$$m = N g_L \mu_B \bar{J}$$

$\alpha << 1 : \frac{E_{mag}}{kT} << 1$

Expand $\mathcal{L}$ $\quad \bar{J} = \frac{J+\frac{1}{2}}{J} \cdot \left(\frac{1}{2\alpha(J+\frac{1}{2})} + \frac{\alpha(J+\frac{1}{2})}{3} \right)$

$$- 2\frac{1}{J}\left(2\frac{1}{2\alpha} + \frac{\alpha}{6} \right)$$

$$= 3\frac{\alpha}{J}\left((J+\tfrac{1}{2})^2 - \tfrac{1}{4} \right)$$

$$= \frac{\alpha}{3J}\left(J(J+1) \right)$$

$$\chi = \frac{N g_L \mu_B}{H_z} \frac{\alpha}{3} \left[J(J+1) \right] = \frac{N}{kT} \frac{(g_L \mu_B)^2}{3} \left[J(J+1) \right]$$

$$m = \frac{H_z N}{kT} \frac{(\mu_B g_L)^2}{3} \left(J(J+1) \right)$$

Problem: Get the classical expression:

a) By $J = \infty$, but μ finite

b) By integrating over $\vec{\mu} \cdot \vec{H}$

Jan 22

Permanent Moments

Ref. Van Vleck ; Seitz

Classically

$$\bar{p} = \sum_i e_i \bar{r}_i$$

Q. M.

$$\langle \bar{p} \rangle = (n | \sum_i e \bar{r} | n)$$

$$+ 2 \mathcal{E} \sum_m \frac{(n|\Sigma er|m)(m|\Sigma er|n)}{E_n - E_m}$$

$(n|\sum_i e_i r_i|n)$ is the permanent moment of a molecule.

$2 \mathcal{E} \sum_m \frac{(n|\Sigma er|m)(m|\Sigma er|n)}{E_n - E_m}$ is the induced magnetic moment. This moment is independent of the temperature if $E_n - E_m << kT$

Parity

$$O \equiv \left\{ \begin{matrix} x \to -x \\ y \to -y \\ z \to -z \end{matrix} \right\}$$ An operation on the coordinate system.

Application of O to a physical quantity can make no difference

$$O\langle\bar{p}\rangle = \langle\bar{p}\rangle$$

However

$$O\psi = \pm\psi$$

$$\langle\bar{p}\rangle = O\langle\bar{p}\rangle = \int O\psi\, O\Sigma e\bar{r}\, O\psi\, d\tau$$

$$= \int \pm\psi - \Sigma e\bar{r} \pm\psi\, d\tau = -\langle\bar{p}\rangle$$

$$\therefore \quad \langle\bar{p}\rangle = 0$$

This tells us that the ground state of an atom (molecule) which possess a permanent el. moment must be degenerate: i.e. it must contain a mixture of wave functions of different parity.

The magnetic moment is an axial vector and does not change sign under O. Hence the parity does not forbid a magnetic moment.

Classical Magnetic Susceptibility

$$\bar{m} = e \sum_i \bar{r}_i \times \bar{p}_i$$

$$= \sum_k \bar{\alpha}_k(q)\, \dot{q}_k$$

{Classical theories do not work. One needs Q. M. for stability.}

$$\bar{m} = A \int d\tau\, e^{-\frac{H(pq)}{\theta}} \sum_k \bar{\alpha}_k(q)\, \dot{q}_k$$

$$\dot{q}_k = \frac{\partial H}{\partial p_k}$$

$$\bar{m} = A \int d\tau \sum_k \left(-\theta \frac{\partial}{\partial p_k} e^{-\frac{H}{\theta}}\right) \bar{\alpha}_k$$

Integrate with respect to p_f

$$\bar{m} = A \int dq\, dp \frac{\partial}{\partial p_f} \left[-\theta e^{H/\theta} \right] \bar{\alpha}_f$$

$$+ A \int d\tau \sum_{k \neq f} \left(-\theta e^{H/\theta} \right) \bar{\alpha}_k$$

But $-\theta e^{-H/\theta} \Big|_{p_{min}}^{p_{max}} = 0$

Hence $\bar{m} = 0$ Classically there is no magnetic moment

Diamagnetism

$$H = \frac{1}{2m} \left(\bar{p} + \frac{e}{c} \bar{A} \right)^2 + \sum \frac{e}{mc} \bar{\sigma} \cdot \nabla \times \bar{A}$$

Let $A = \frac{H_2 \times r}{2}$

$$A_x = -H_2 \frac{y}{2}$$
$$A_y = H_2 \frac{x}{2}$$
$$A_z = 0$$

$$H = \frac{p^2}{2m} + \frac{1}{2m} 2 \frac{e}{c} \frac{H_2}{2} (-y p_x + p_y x)$$

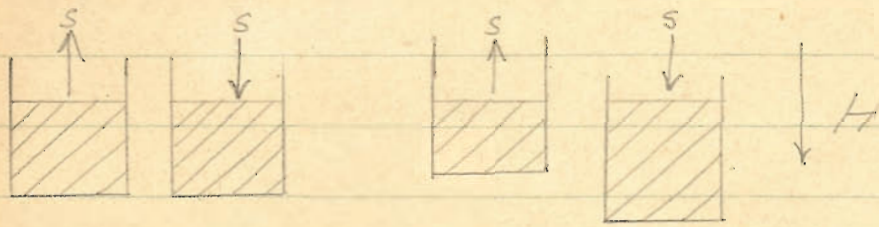
$$+ \frac{1}{2m} \frac{e^2}{c^2} \frac{H_2^2}{4} (x^2 + y^2) + \frac{e}{mc} \bar{\sigma} \cdot \bar{H}$$

The diamagnetic term is

$$\frac{1}{2m}\frac{e^2}{c^2}\frac{H_z^2}{4}(x^2+y^2)$$

$$m_z = -\frac{\partial E}{\partial H_z} = -\frac{e^2}{4mc^2}H_z\frac{2}{3}n\overline{r^2}\cdot N$$

A Fermi Gas of electrons is paramagnetic



No field H field