

Back to Stat Mech.

Microcanonical ensemble

In ~~an~~ equilibrium, ^{isolated} system is equally likely to be in any one of its accessible states.

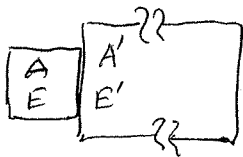
$$P(r) = \begin{cases} \frac{1}{\Omega} & \text{if } E < E_r < E + \Delta E \\ 0 & \text{otherwise} \end{cases}$$

$\Omega = \#$ of accessible states

$$S = k \ln \Omega$$

} Microcanonical ensemble
Good for isolated systems

What about systems in contact with a heat reservoir?



In equilibrium what is probability P_r of finding A in any one microstate r w/ energy E_r ?

r - quantum state
($q_1, \dots, q_j, p_1, \dots, p_j$)

$$A^0 = A + A'$$

$$E^0 = E_r + E'$$

What is probability distribution for microstates?

Found previously $P(r) \propto \Omega'(E^0 - E_r)$

Since heat bath is large & $E_r \ll E^0$ we can expand around E^0

$$\ln \Omega'(E^0 - E_r) = \ln \Omega'(E^0) - \left. \frac{\partial \ln \Omega'}{\partial E'} \right|_{E'=E^0} E_r + \dots$$

neglect higher order terms

$$\frac{\partial \ln \Omega'}{\partial E'} = \beta' = \frac{1}{kT_{\text{bath}}}$$

$P(r) \propto e^{-\beta' E_r}$ usually we drop the "prime" & remember that β is for bath

Let's go beyond proportionality & normalize the distribution

[WORKING ON ...]

Normalization

Discrete

$$P(r) = \frac{e^{-\beta E_r}}{Z}$$

Geometrical
Distribution

Z is the "Zustandsumme"
Sum over states
also called the partition function

$$\bar{y} = \frac{\sum_r y e^{-\beta E_r}}{Z}$$

$$Z = \sum_r e^{-\beta E_r}$$

Boltzmann
factor

Continuum

$$P(q,p) d^3q d^3p = \frac{e^{-\beta E} d^3q d^3p}{\int e^{-\beta E} d^3q d^3p}$$

$$Z = \int e^{-\beta E} d^3q d^3p$$

$$\bar{y} = \frac{\int y e^{-\beta E(q,p)} d^3q d^3p}{\int e^{-\beta E(q,p)} d^3q d^3p}$$

Ex: Ideal gas

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

$$P(q,p) d^3q d^3p = \frac{e^{-\beta \left(\frac{p^2}{2m}\right)} d^3q d^3p}{\int e^{-\beta \left(\frac{p^2}{2m}\right)} d^3q d^3p}$$

} Maxwell distribution

Lets add some pizzaz!

ideal gas of colloids + gravity

$E = ?$

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

$$P(q,p) d^3q d^3p = \frac{e^{-\beta \left(\frac{p^2}{2m} + mgz\right)} d^3q d^3p}{\int e^{-\beta \left(\frac{p^2}{2m} + mgz\right)} d^3q d^3p}$$

$$P(z) dz = \frac{\int_{x,y} \int_{\vec{p}} P(q,p) d^3q d^3p}{\int_{x,y} \int_{\vec{p}} e^{-\beta \left(\frac{p^2}{2m} + mgz\right)} d^3q d^3p} = C' e^{-\beta mgz} dz$$

$$P(z) = P(0) e^{-mgz/hT}$$

410 Experiment

$$\bar{E} = \frac{\sum_r E_r e^{-\beta E_r}}{\sum_r e^{-\beta E_r}} \quad \text{or}$$

$$\bar{E} = \frac{\int E(\Omega, \beta) e^{-\beta E} d^3 \Omega d^3 p}{\int e^{-\beta E} d^3 \Omega d^3 p}$$

$$\sum_r e^{-\beta E_r} E_r = - \sum_r \frac{\partial}{\partial \beta} e^{-\beta E_r} = - \frac{\partial}{\partial \beta} (z)$$

Same trick we used for the Binomial dist.

$$\bar{E} = - \frac{1}{z} \frac{\partial z}{\partial \beta} = - \frac{\partial \ln z}{\partial \beta}$$

instead of $\frac{\partial \ln \Omega(E)}{\partial E}$

this makes things alot easier since z is a sum over all possible energies where $\Omega(E)$ is the sum of states w/ $E < E_r < E_r + \delta E$

$$\overline{E^2} = \frac{\sum_r E_r^2 e^{-\beta E_r}}{\sum_r e^{-\beta E_r}}$$

$$\sum_r e^{-\beta E_r} E_r^2 = - \frac{\partial}{\partial \beta} (\sum_r e^{-\beta E_r} E_r) = \left(- \frac{\partial}{\partial \beta} \right)^2 \sum_r e^{-\beta E_r}$$

same trick we used for Binomial dist.

$$\overline{E^2} = \frac{1}{z} \frac{\partial^2 z}{\partial \beta^2} = \frac{\partial}{\partial \beta} \left(\frac{1}{z} \frac{\partial z}{\partial \beta} \right) + \frac{1}{z^2} \left(\frac{\partial z}{\partial \beta} \right)^2 = - \frac{\partial \bar{E}}{\partial \beta} + \overline{E^2}$$

$$\overline{E^2} - \bar{E}^2 = - \frac{\partial \bar{E}}{\partial \beta} = \frac{\partial^2 \ln z}{\partial \beta^2}$$

More generally:

Note to self: $\frac{\partial \ln z}{\partial x} \neq \frac{\partial}{\partial x} \left(\frac{\sum_r e^{-\beta E_r}}{\sum_r e^{-\beta E_r}} \right)$ since $\ln(a+b) \neq \ln a + \ln b$

~~$$\frac{\partial \ln z}{\partial x} = \frac{\partial}{\partial x} \left(\frac{\sum_r e^{-\beta E_r}}{\sum_r e^{-\beta E_r}} \right)$$~~

$$dW = \bar{X} dx \quad \bar{X} = - \frac{\partial E_r}{\partial x} = \frac{\sum_r e^{-\beta E_r} \left(- \frac{\partial E_r}{\partial x} \right)}{\sum_r e^{-\beta E_r}}$$

$$\sum_r e^{-\beta E_r} \frac{\partial E_r}{\partial x} = - \frac{1}{\beta} \frac{\partial}{\partial x} (\sum_r e^{-\beta E_r}) = - \frac{1}{\beta} \frac{\partial z}{\partial x}$$

$$\bar{X} = + \frac{1}{\beta z} \frac{\partial z}{\partial x} = \frac{1}{\beta} \frac{\partial \ln z}{\partial x}$$

$$\text{Ex: } dW = \bar{p} dV = \frac{1}{\beta} \frac{\partial \ln z}{\partial V} dV$$

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

Connection to thermodynamics

$$Z = Z(\beta, X)$$

$$d \ln Z = \frac{\partial \ln Z}{\partial X} dX + \frac{\partial \ln Z}{\partial \beta} d\beta$$

$$= \beta dW - \bar{E} d\beta = \beta dW - d(\beta E) + \beta dE$$

$$= d(\ln Z + \beta E) = \beta(dE + dW) = \beta dQ$$

$$S = k(\ln Z + \beta E) \quad \text{or} \quad TS = kT \ln Z + E$$

$$E - TS = \boxed{F = -kT \ln Z}$$

Contact with a thermal bath

also

$$S = k \ln Z + kT \left. \frac{d \ln Z}{dT} \right|_V$$

~~ended lost time~~

←
ended
lost time

$$\left. \frac{\partial F}{\partial T} \right|_V = -k \ln Z + \frac{d \ln Z}{T \partial \beta}$$

used $\beta = \frac{1}{kT}$
 $d\beta = -\frac{1}{kT^2} dT$

$$= -k(\ln Z + \beta E) = -S \quad \checkmark$$

$$\left. \frac{\partial F}{\partial V} \right|_T = \frac{\partial}{\partial V} (-kT \ln Z) = -kT \frac{\partial \ln Z}{\partial V} = -P \quad \checkmark$$

Note: this definition of entropy $S = k(\ln Z + \beta E)$ involves knowledge of Z rather than Ω . Computing Z is usually simpler since it involves an unrestricted sum or integral over all states whereas a computation of $\Omega(E)$ involves the difficult problem of counting only the states w/ Energies

$$E < E_r < E + \delta E$$

Also note that the entropy does not depend on the size of ~~the~~ our energy interval δE

Grand Canonical Ensemble

Exchange of Energy (Temp, volume, etc.) & # of particles

$$E + E' = E^0 = \text{const}$$

$$N + N' = N^0 = \text{const}$$

$$P_r(E_r, N_r) \propto \Omega'(E^0 - E_r, N^0 - N_r)$$

Taylor Expand around E^0 & N^0

$$\ln \Omega' = \ln \Omega'(E^0 - E_r, N^0 - N_r) = \ln \Omega'(E^0, N^0) - \left. \frac{\partial \ln \Omega'}{\partial E'} \right|_{E'=E^0} E_r - \left. \frac{\partial \ln \Omega'}{\partial N'} \right|_{N'=N^0} N_r$$

$$\beta = \left. \frac{\partial \ln \Omega'}{\partial E'} \right|_{E'=E^0} \quad \alpha = \left. \frac{\partial \ln \Omega'}{\partial N'} \right|_{N'=N^0}$$

$$\Omega'(E^0 - E_r, N^0 - N_r) = \Omega'(E^0, N^0) e^{-\beta E_r - \alpha N_r}$$

$P_r \propto e^{-\beta E_r - \alpha N_r}$
Grand Canonical distribution

$\mu = -kT\alpha$ so α is related to the chemical potential

Discrete (QM)

$$\bar{E} = \frac{\sum_r e^{-\beta E_r - \alpha N_r} E_r}{\sum_r e^{-\beta E_r - \alpha N_r}}$$

$$\bar{N} = \frac{\sum_r e^{-\beta E_r - \alpha N_r} N_r}{\sum_r e^{-\beta E_r - \alpha N_r}}$$

Continuum (classical)

$$\bar{E} = \frac{\int e^{-\beta E - \alpha N} E d^3q d^3p}{\int e^{-\beta E - \alpha N} d^3q d^3p}$$

$$\bar{N} = \frac{\int e^{-\beta E - \alpha N} N d^3q d^3p}{\int e^{-\beta E - \alpha N} d^3q d^3p}$$

Connection to Thermodynamics

$$\bar{E} = -\frac{d \ln \Xi}{d\beta} \quad \Xi = \sum_r e^{-\beta E_r - \alpha N_r} = \sum_r z e^{\beta \mu N_r}$$

$$\bar{N} = \frac{1}{\Xi} \frac{d \Xi}{d\alpha} = -\frac{d \ln \Xi}{d\alpha}$$

$$\Xi = \Xi(\beta, x, N) \quad dQ = dE + dw - \mu dN \quad \mu \Xi = \frac{-\alpha}{\beta}$$

$$d \ln \Xi = \frac{d \ln \Xi}{dx} dx + \frac{d \ln \Xi}{d\beta} d\beta + \frac{d \ln \Xi}{d\alpha} d\alpha$$

$\underbrace{\frac{d \ln \Xi}{dx}}_{\beta dw} \quad \underbrace{\frac{d \ln \Xi}{d\beta}}_{-E} \quad \underbrace{\frac{d \ln \Xi}{d\alpha}}_{-N}$

$$d \ln \Xi = \beta dw - d(\beta E) + \beta dE - d(\alpha N) + \alpha dN$$

$$d(\ln \Xi + \beta E + \alpha N) = \beta da \quad ds = \frac{dq}{T}$$

$$S = k(\ln \Xi + \beta E + \alpha N) = k \ln \Xi + kT \left. \frac{d \ln \Xi}{dT} \right)_{V, \mu}$$

$$TS = kT \ln \Xi + E - \mu N$$

$$\underbrace{E - TS - \mu N}_{\text{Grand Canonical potential}} = -kT \ln \Xi$$

Grand Canonical potential
Legendre transform of G

Can also show:

$$\overline{N^2} - \bar{N}^2 = (kT)^2 \left. \frac{\partial^2 \ln \Xi}{\partial \mu^2} \right)_{V, T}$$

$$\overline{E^2} - \bar{E}^2 = \left. \frac{\partial^2 \ln \Xi}{\partial \beta^2} \right)_{V, \mu}$$

Getting to know Z

Technically speaking, for our continuum calculations we need to normalize d^3q, d^3p by h^3

$$Z = \int e^{-\beta E(q_1, \dots, q_j, p_1, \dots, p_j)} \frac{dq_1, \dots, dp_j}{h^3}$$

I usually drop this factor since we have it in the Numerator & denominator

Additive Constants to Energy

$$E_r^* = E_r + \epsilon_0 \leftarrow \text{added Const.}$$

$$Z^* = \sum_r e^{-\beta(E_r + \epsilon_0)} = \sum_r e^{-\beta E_r} e^{-\beta \epsilon_0} = e^{-\beta \epsilon_0} Z$$

$$\ln Z^* = \ln Z - \beta \epsilon_0$$

$$\bar{E}^* = -\frac{d \ln Z^*}{d\beta} = -\frac{d \ln Z}{d\beta} + \epsilon_0 = \bar{E} + \epsilon_0 \quad \checkmark$$

$$S^* = k(\ln Z^* + \beta \bar{E}^*) = k(\ln Z + \beta \bar{E}) = S \quad \checkmark$$

So just changing the energy does not change S

Non interacting systems ex: two ideal gas systems

$$E^0 = E_r + E_s'$$

$$Z^0 = \sum_{r,s'} e^{-\beta(E_r + E_s')} = \sum_{r,s} e^{-\beta E_r} e^{-\beta E_s'} = \sum_r e^{-\beta E_r} \sum_s e^{-\beta E_s'}$$

$$Z^0 = Z Z'$$

$$\ln Z^0 = \ln Z + \ln Z'$$

If a system consists of distinct non interacting parts

Z factors into a simple product of the Z 's for the individual parts

EX: ideal gas

$$E = \sum_i \frac{p_i^2}{2m}$$

$$z^0 = \int e^{-\beta E} \frac{d^3q_1, \dots, d^3q_N, d^3p_1, \dots, d^3p_N}{h^{3N}}$$

$$z^0 = \frac{V^N}{h^{3N}} \int e^{-\beta \frac{p_1^2}{2m}} d^3p_1 \dots \int e^{-\beta \frac{p_N^2}{2m}} d^3p_N$$

$$\zeta \equiv \frac{V}{h^{3/2}} \int_{-\infty}^{\infty} e^{-\beta \frac{1}{2m} p^2} d^3p \quad p^2 = p_x^2 + p_y^2 + p_z^2$$

partition function
for a single molecule

$$z^0 = \zeta^N = \left[V \left(\frac{2\pi m}{h^2 \beta} \right)^{3/2} \right]^N$$

$$\ln z^0 = N \left[\ln V - \frac{3}{2} \ln \beta + \frac{3}{2} \ln \left(\frac{2\pi m}{h^2} \right) \right]$$

$$\bar{p} = \frac{1}{\beta} \frac{d \ln z}{dV} = \frac{1}{\beta} \frac{N}{V}$$

$$pV = NkT \quad \checkmark$$

$$\bar{E} = - \frac{d \ln z}{d\beta} = \frac{3}{2} \frac{N}{\beta} = \frac{3}{2} NkT \quad \checkmark$$

$$C_V = \left(\frac{\partial E}{\partial T} \right)_V = \frac{3}{2} Nk \quad C_V = \frac{3}{2} R \quad \checkmark$$

$$S = k (\ln z^0 + \beta E)$$

$$S = Nk \left(\ln V - \frac{3}{2} \ln \beta + \frac{3}{2} \ln \frac{2\pi m}{h^2} + \frac{3}{2} \right)$$

Const

This is a problem

Gibbs Paradox

S is extensive!

$$S^0 = S + S'$$

S	S'
V/N	V'/N'

two identical
systems

$$S = S' = Nk \left[\ln V + \frac{3}{2} \ln T + \text{Const} \right]$$

$$S^0 = 2Nk \left[\ln 2V + \frac{3}{2} \ln T + \text{Const} \right]$$

$$S^0 - 2S = 2Nk \left[\ln 2V + \frac{3}{2} \ln T + \text{Const} \right] - 2Nk \left[\ln V + \frac{3}{2} \ln T + \text{Const} \right] \\ = 2Nk \ln 2 \neq 0$$

What went wrong:

We used a classical description where we assumed each particle was distinguishable & so upon removal of the partition the particles mix. But for indistinguishable particles mixing doesn't mean anything

If the two gases are different, removing the partition increases the entropy due to mixing of the gases (irreversible)

If the two gases are identical removing the partition is a reversible process!

interchanging the positions of two atoms leaves us w/ the same system

For N particles there are $N!$ different arrangements that we overcounted

$$Z = \frac{\zeta^N}{N!}$$

$$\ln Z = N \ln \zeta - \ln N!$$

using Stirling's formula
this gives

$$= N \ln \zeta - N \ln N + N$$

what happens to P & E ?

$\frac{\partial}{\partial \beta}$ & $\frac{\partial}{\partial V}$ do not care about extra factor of

$-N \ln N + N$ so these results stay the same

what about S ?

$$S = kN \left[\ln V + \frac{3}{2} \ln T + \text{const} \right] + k[-N \ln N + N]$$

$$S = kN \left[\ln \left(\frac{V}{N} \right) + \frac{3}{2} \ln T + \text{const} \right]$$

so now $N \rightarrow 2N$ but $\frac{V}{N}$ stays the same
 $V \rightarrow 2V$

$$S^0 - 2S = 0$$

Note: This description still breaks down as $T \rightarrow 0$ since

$\lim_{T \rightarrow 0} \ln T = -\infty$ before this happens you need to deal w/ quantum nature of the particles.

Equipartition Theorem Classical

If you can write energy as a sum of terms quadratic in p or q then each mode (need integral) gets assigned $\frac{1}{2}kT$

$$E = E(q_1, \dots, q_s, p_1, \dots, p_s)$$

Suppose $E = \epsilon_i(p_i) + E'(q_1, \dots, q_s, p_1, \dots, p_{i-1}, p_{i+1}, \dots, p_s)$

& suppose $\epsilon_i(p_i) = b p_i^2$ works equally well for $\epsilon_i(q) = b q^2$

What is the mean value of ϵ_i in thermal equilibrium?

$$\bar{\epsilon}_i = \frac{\int e^{-\beta E} \epsilon_i dq_1 \dots dp_s}{\int e^{-\beta E} dq_1 \dots dp_s}$$

$$\bar{\epsilon}_i = \frac{\int e^{-\beta \epsilon_i} \epsilon_i dp_i}{\int e^{-\beta \epsilon_i} dp_i} = -\frac{d}{d\beta} \ln \left[\int_{-\infty}^{\infty} e^{-\beta \epsilon_i} dp_i \right]$$

$$\int_{-\infty}^{\infty} e^{-\beta \epsilon_i} dp_i = \int_{-\infty}^{\infty} e^{-\beta b p_i^2} dp_i$$

$$= \beta^{-1/2} \int_{-\infty}^{\infty} e^{-b y^2} dy$$

change variables

$$y = \beta^{1/2} p_i$$

$$dy = \beta^{1/2} dp_i$$

Note that limits do not change if they go from $-\infty \rightarrow \infty$

$$\bar{\epsilon}_i = -\frac{d}{d\beta} \left[-\frac{1}{2} \ln \beta + \ln \int_{-\infty}^{\infty} e^{-b y^2} dy \right]$$

$$= \frac{1}{2\beta} = \frac{1}{2} kT$$

works for $\epsilon_i = b q^2$ as well

Examples:

Kinetic energy $K = \frac{(p_x^2 + p_y^2 + p_z^2)}{2m}$

$$\bar{k} = \frac{3}{2} kT$$

$$\bar{E} = N \bar{k} = \frac{3}{2} N kT = \frac{3}{2} RT$$

$$C_v = \left(\frac{\partial \bar{E}}{\partial T} \right)_v = \frac{3}{2} R$$

Brownian motion

$$\bar{v}_x = 0$$

$$\frac{1}{2} m \overline{v_x^2} = \frac{1}{2} kT$$

$$\overline{v_x^2} = \frac{kT}{m}$$

as mass of particle decreases you get fluctuation in velocity - This is Brownian motion

Harmonic oscillator

$$E = \frac{p^2}{2m} + \frac{1}{2} k x^2$$

$$1-D \quad \bar{E} = \frac{1}{2} kT + \frac{1}{2} kT = kT$$

$$3D \quad \bar{E} = \frac{3}{2} kT + \frac{3}{2} kT = 3kT$$

Do the classical approximation
match up w/ QM descriptions at high T?

$$E_n = \left(n + \frac{1}{2}\right) \hbar \omega$$

$$n = 0, 1, 2, 3 \dots$$

$$\omega = \sqrt{\frac{k_0}{m}}$$

$$\bar{E} = -\frac{d \ln Z}{d\beta}$$

$$Z = \sum_{n=0}^{\infty} e^{-\beta E_n} = \sum_{n=0}^{\infty} e^{-\beta \hbar \omega (n + \frac{1}{2})} = e^{-\frac{1}{2} \beta \hbar \omega} \sum_{n=0}^{\infty} e^{-n \beta \hbar \omega}$$

$$= e^{-\frac{1}{2} \beta \hbar \omega} (1 + e^{-\beta \hbar \omega} + e^{-2\beta \hbar \omega} + \dots) \quad \text{infinite geometric series}$$

$$Z = \frac{e^{-\frac{1}{2} \beta \hbar \omega}}{(1 - e^{-\beta \hbar \omega})}$$

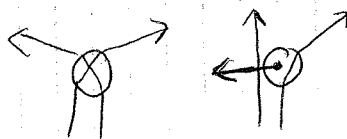
$$\ln Z = -\frac{1}{2} \beta \hbar \omega - \ln(1 - e^{-\beta \hbar \omega})$$

$$E = -\frac{d \ln Z}{d\beta} = -\left(-\frac{1}{2} \hbar \omega - \frac{\hbar \omega e^{-\beta \hbar \omega}}{1 - e^{-\beta \hbar \omega}}\right) = \boxed{\hbar \omega \left(\frac{1}{2} + \frac{1}{e^{\beta \hbar \omega} - 1}\right)}$$

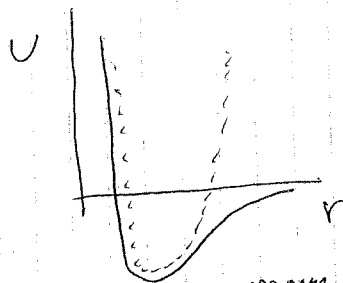
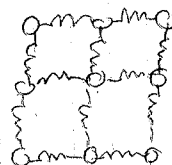
limits: $\frac{\hbar \omega}{kT} \ll 1$ high Temp where we should approach classical limit

$$\bar{E} = \hbar \omega \left(\frac{1}{2} + \frac{1}{(1 + \beta \hbar \omega + \dots) - 1}\right) = \hbar \omega \left(\frac{1}{2} + \frac{1}{\beta \hbar \omega}\right) \approx \frac{\hbar \omega}{\beta \hbar \omega} = kT \quad \checkmark$$

Ex. Colloids in an optical trap



atoms



Bottom of ~~the~~ ^{many} potentials
can be approx by a
harmonic oscillator potential

limit $\frac{hw}{kT} \gg 1$

$$\bar{E} = hw \left(\frac{1}{2} + e^{-\beta hw} \right) \quad \text{as } T \rightarrow 0 \quad e^{-\beta hw} \rightarrow 0$$

$$\text{so } \bar{E}_{T \rightarrow 0} \rightarrow \frac{hw}{2}$$

Specific heat of Solids (~~Einstein Model~~)

Consider atoms on a lattice w/ SHO potential

$$E = \sum_{i=1}^{3N} \frac{p_i^2}{2m} + \frac{1}{2} k_i q_i^2 = 3N kT = 3RT \quad \text{for } N = N_A$$

$$C_V = \left(\frac{\partial E}{\partial T} \right)_V = 3R$$

25 Joules/mol deg low of Dulong & Petit

	C_p (J/mol deg)
Copper	24.5
Silver	25.5
Lead	26.4
...	
Tin	26.4
Sulphur	22.4
Carbon	6.1

at low T we need QM (Einstein Model) Assume all atoms vibrate at same freq

$$\bar{E} = 3Nhw \left(\frac{1}{2} + \frac{1}{e^{\beta hw} - 1} \right)$$

$$C_V = \left(\frac{\partial \bar{E}}{\partial T} \right)_V = \frac{\partial \bar{E}}{\partial \beta} \frac{d\beta}{dT} = -\frac{1}{kT^2} \left(\frac{\partial \bar{E}}{\partial \beta} \right)_V$$

$$= -\frac{3Nhw}{kT^2} \left[\frac{-e^{\beta hw} hw}{(e^{\beta hw} - 1)^2} \right]$$

$\Theta_E \equiv \frac{hw}{k}$ Einstein Temp

$$C_V = 3R \left(\frac{\Theta_E}{T} \right)^2 \left[\frac{e^{\Theta_E/T}}{(e^{\Theta_E/T} - 1)^2} \right]$$

for $N = N_A$

if $T \gg \Theta_E \quad C_V \rightarrow 3R$

if $T \ll \Theta_E \quad C_V \rightarrow 3R \left(\frac{\Theta_E}{T} \right)^2 e^{-\Theta_E/T} \quad \text{As } T \rightarrow 0 \quad C_V \rightarrow 0$

Experimentally $C_V \propto T^3$ discrepancy comes from assumption that all atoms vibrate at same frequency

Before QM it was not understood why the specific heat of some solids like Carbon fell below the classical equipartition value of 3R at low T. Einstein's 1907 theory helped gain acceptance for the new quantum concepts