Lecture 4

Lattice

n interstitial sites $\quad E(n) = n\varepsilon$

which lattice sites are empty?

$\frac{N!}{n!(N-n)!}$ a number of ways to empty the lattice sites

$\Omega(n) = \left(\frac{N!}{n!(N-n)!}\right)^2$ product of the two

Maximize the total entropy of the system

$$\frac{1}{T} = \frac{\partial S}{\partial E} = \frac{\partial S}{\partial n}\frac{\partial n}{\partial E} = \frac{1}{\varepsilon}\frac{\partial S}{\partial n}$$

Consider a system in equilibrium with a heat bath

$$P_r = \frac{1}{Z} e^{-\beta E_r} \qquad \langle E \rangle = \sum_r E_r p_r = -\frac{\partial \ln Z}{\partial \beta}$$

~~$\langle E \rangle = \sum_r E_r p_r = \partial n$~~ $\quad (\Delta E)^2 = (E - \bar{E})^2 = \langle E^2 \rangle - \langle E \rangle^2 = \frac{\partial^2 \ln Z}{\partial \beta^2} = -\frac{\partial \langle E \rangle}{\partial \beta}$

$$= -\frac{\partial \langle E \rangle}{\partial T}\frac{\partial T}{\partial \beta} = k C_v T^2$$

$T = \frac{1}{k\beta}$

$\frac{\partial T}{\partial \beta} = -\frac{1}{k\beta^2} = -\frac{1}{k} k^2 T^2 = kT^2$ →

$\Delta E = \sqrt{k}\, T \sqrt{C_v}$

$\frac{\Delta E}{E} = \sqrt{k}\, T \frac{\sqrt{C_v}}{\langle E \rangle}$ } extensive variables ratio $\propto \frac{1}{\sqrt{N}} \sim 10^{-11}$ for macroscopic systems

$\frac{\Delta E}{E} \propto \frac{1}{\sqrt{N}}$ the fluctuations of energy are extremely small!

$$P(E)\,dE = \frac{1}{Z} e^{-\beta E} f(E)\,dE \propto \underbrace{e^{-\beta E} E^{3N/2 - 1}}_{\text{trade off of domination for } N}$$

$f(E)$: number of quantum states

The energy of a system is constant. $S = k \ln \Omega$ under general definition of entropy. Boltzmann's equation only works for constant E.

Gibb's Ensemble

ν identical systems with the same constraints is a constant

with a heat bath can apply any constraint $\nu \to \infty$

$\nu_r = \nu p_r$ ν different states

micro macro

Energy of the ensemble: $E = \sum_r \nu_r E_r = \sum_r \nu p_r E_r$ = fixed quantity

$\boxed{\nu_1 \mid \nu_2 \mid \nu_3 \mid \cdots}$ the number of ways of writing ν objects $= \nu!$

Ω_ν ← ν_1 can be placed in $\nu!$ ways

$\Omega_\nu \, \nu_1! \, \nu_2! \, \nu_3! \cdots \nu_n! = \nu!$

$$\Omega_\nu = \frac{\nu!}{\prod_r \nu_r!}$$

Same as formula for N objects $\frac{N!}{n!(N-n)!}$

generalization of

$$S_\nu = k \ln \Omega_\nu = k \ln \left(\frac{\nu!}{\prod_r \nu_r!} \right) \qquad S(E) = \frac{S_\nu}{\nu}$$ identical systems of weakly interacting w/ eachother

$$S_\nu = k \left[\ln \nu! - \sum_r \ln \nu_r! \right]$$

$\nu \to \infty$ $S_\nu = k \left[\nu \ln \nu - \nu - \sum_r (\nu_r \ln \nu_r - \nu_r) \right] \longrightarrow -\nu k \sum_r p_r \ln p_r$

$= k \left\{ \nu \ln \nu - \nu \sum_r p_r (\ln \nu + \ln p_r) \right\}$ using $\nu_r = \nu p_r$

$= k \left\{ \nu \ln \nu - \nu \ln \nu \cancel{\sum_r p_r} - \nu \sum_r p_r \ln p_r \right\}$ (the $\sum p_r = 1$)

General Definition of Entropy

$$\boxed{S = \frac{1}{\nu} S_\nu = -k \sum_r p_r \ln p_r}$$

derived from Boltzmann's apply ensemble with fixed E

NOTE BOOK

Lecture 4 continued...

When in thermal equilibrium w/ heat bath with the number of particles in the system being constant

$$p_r = \frac{1}{Z} e^{-\beta E_r}$$

$$S = -k \sum_r \frac{e^{-\beta E_r}}{Z} \left(-\beta E_r - \ln Z\right) = -k \sum_r p_r \left(-\beta E_r - \ln Z\right)$$

$$= k\beta \underbrace{\sum_r p_r E_r}_{=\langle E \rangle} + k \ln Z \underbrace{\sum_r p_r}_{=1} = \frac{\langle E \rangle}{T} + k \ln Z$$

$$\boxed{S = \frac{\langle E \rangle}{T} + k \ln Z}$$

dimensions of J/K

expression of entropy of system in thermal eq. with heat bath

* If you know Z, you can get an thermodynamic property

eg $\langle E \rangle = -\frac{\partial \ln Z}{\partial \beta}$

Helmholtz free energy

$$F = \underbrace{\langle E \rangle - TS}_{\text{use to minimize } F} = \underbrace{-kT \ln Z}_{\text{do not use this expression to minimize } F \text{ it already is!}}$$

Derive Boltzmann's Equation

Fundamental Postulate: All microstates are equally probable

① $p_r = \frac{1}{\Omega}$

② $S = -k \sum_r p_r \ln p_r$ = general expression of S

$$S(E) = -k \sum_r \frac{\ln\left(\frac{1}{\Omega}\right)}{\Omega} = +k \sum_r \left(\frac{\ln \Omega}{\Omega}\right) \equiv k \ln \Omega \sum p_r = k \ln \Omega$$

NOTE BOOK

Diamagnetic - $\vec{\mu}$ is induced by external field
Paramagnetic - material where each atom has a permanent magnetic dipole moment $\vec{\mu}$
if the currents of e^- around don't cancel $\Rightarrow \vec{\mu}$
add vectorally the orbital motion of e^- $\vec{\mu}_L$
Spin magnetic $\vec{\mu}_S$

Spin $\vec{\mu}_S \propto \frac{1}{\text{mass}}$ proton spin is ~ 1000x smaller

hydrogen has a magnetic moment due to spin

helium atom $\vec{\mu} = 0 \therefore$ diamagnetic

atoms on a lattice - each has $\hbar/2$ integral spin ang. mom.

o o o o
o o o o
o o o o

$\vec{\mu} \propto \vec{J}$
$\vec{\mu} = g\vec{J}$
$\mu_z = g J_z$
$= \pm \frac{g\hbar}{2} = \pm \mu$

} the value of $\frac{J}{=}$ varies in steps between $\pm J$

Hydrogen atom $\mu = \frac{e\hbar}{2m}$ m = mass of electron

orbital angular momentum can't take $\hbar/2$ so when $\hbar/2$ there must be spin involved.

$m_e = 9.11 \cdot 10^{-31}$ kg
$m_p = 1.67 \cdot 10^{-27}$ kg
$e = 1.6 \cdot 10^{-19}$ C

place a paramagnetic solid in an external field $\vec{\mu}_{net} \neq 0$

$\vec{\tau} = \vec{\mu} \times \vec{B}$ torque orients } competition
the thermal vibrations act against $\vec{\tau}$ }

$\vec{\mu}_{net}$ = function of temperature
Curie's Law: For small T $\vec{\mu}_{net} \propto \frac{1}{T}$

When you chose the system heat bath approx - trick is to be able to calculate quantum states