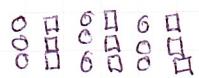


Lecture 4

Lattice



n interstitial sites

$$E(n) = n \epsilon$$

which lattice sites are empty?

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

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

Maximize the total entropy of the system

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

Consider a system in equilibrium with a heat bath

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

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

$$T = \frac{1}{k\beta} \quad = -\frac{\partial \langle E \rangle}{\partial T} \frac{\partial T}{\partial \beta} = k C_v T^2$$

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

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

$$\frac{\Delta E}{E} = \sqrt{k T} \frac{\sqrt{C_v}}{\langle E \rangle} \quad \left. \begin{array}{l} \text{extensive variables ratio} \propto \frac{1}{\sqrt{N}} \\ \text{of energy} \end{array} \right\} \sim 10^{-11} \text{ for macroscopic systems}$$

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

$$P(E) dE = \frac{1}{Z} e^{-\beta E} f(E) dE \propto e^{-\beta E} E^{3N/2 - 1}$$

in
 number of
 quantum
 states

trade off of domination for N

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 $\nu \rightarrow \infty$

$$\nu_r = \nu p_r \quad \nu \text{ different states}$$

↑ ↑
micro micro

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

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

Ω_ν ν_r can be placed in $\nu!$ ways

$$\Omega_\nu \nu_1! \nu_2! \nu_3! \dots \nu_n! = \nu!$$

$$\Omega_\nu = \frac{\nu!}{\prod_r \nu_r!} \quad \begin{matrix} \text{Same as formula} \\ \text{for } N \text{ objects} \end{matrix} \quad \frac{\nu!}{n!(\nu-n)!}$$

$\xrightarrow{\text{generalization of}}$

$$S_\nu = k \ln \Omega_\nu = k \ln \left(\frac{\nu!}{\prod_r \nu_r!} \right)$$

$S(E) = \frac{S_\nu}{\nu}$ identical systems
of weakly interacting
w/ each other

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

$$\begin{aligned} \nu \rightarrow \infty \quad S_\nu &= k \left[\nu \ln \nu - \nu - \sum_r (\nu_r \ln \nu_r - \nu_r) \right] \rightarrow -\nu k \sum_r p_r \ln p_r \\ &= k \left\{ \nu \ln \nu - \nu \sum_r p_r (\ln \nu + \ln p_r) \right\} \quad \text{using} \\ &= k \left\{ \nu \ln \nu - \nu \ln \nu \cancel{\sum_r p_r} - \nu \sum_r p_r \ln p_r \right\} \quad \nu_r = \nu p_r \end{aligned}$$

General Definition of Entropy

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

derived from Boltzmann's
apply ensemble with
fixed E

Lecture 4 continued...

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

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

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

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

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

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

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

Helmholtz free energy

$$F = \underbrace{\langle E \rangle}_{\text{use to minimize } F} - TS = -kT \ln Z$$

do not use this expression to minimize F
it already is!

Derive Boltzmann's Equation

Fundamental Postulate: All microstates are equally probable

①

$$p_r = \frac{1}{\Omega}$$

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

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

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 vectorially the orbital motion \vec{J} of e^-
Spin magnetic $\vec{\mu}_s$

Spin $\vec{\mu}_s \propto \frac{1}{\text{mass}}$ proton spin is $\sim 1000\times$ smaller

hydrogen has a magnetic moment due to spin

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

atoms on a lattice - each has $\frac{1}{2}$ integral spin ang. mom.

0 0 0
0 0 0
0 0 0

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

} the value of J varies in steps between $\pm \frac{1}{2} J$

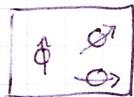
Hydrogen atom $\mu = \frac{e \hbar}{2m}$ m = mass of electron

orbital angular momentum can't take $\frac{1}{2}$ so when $\frac{1}{2}$ there must be spin involved.

$$m_e = 9.11 \cdot 10^{-31} \text{ kg}$$

$$m_p = 1.67 \cdot 10^{-27} \text{ kg}$$

$$e = 1.6 \cdot 10^{-19} \text{ C}$$



place a paramagnetic solid in an external field $\vec{B}_{\text{ext}} \neq 0$

$$\vec{\tau} = \vec{\mu} \times \vec{B} \quad \text{torque orients } \quad \left. \right\} \text{competition}$$

the thermal vibrations act against $\vec{\tau}$

$\vec{\mu}_{\text{net}} = \text{function of temperature}$

$$\text{Curie's Law: For small } T \quad \vec{\mu}_{\text{net}} \propto \frac{1}{T}$$

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