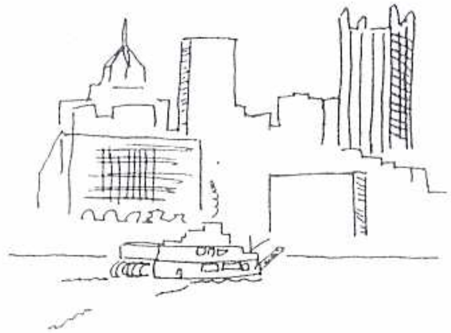


[Jan. 10, 2007]

Statistical mechanics in Action

[I] spin-$\frac{1}{2}$ system in a constant magnetic field [Paramagnet]

$\vec{B}\uparrow \quad \vec{s}\uparrow \quad \hat{z}$ $\qquad E = -\mu_0 S_z B \;;\; S_z = \pm 1$

i.e. $+\mu_0 B$ — $S_z = -1$; E_-

$-\mu_0 B$ — $S_z = +1$; E_+

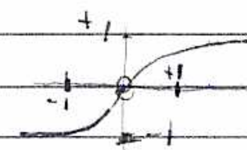
[for $\mu_0 > 0$]

What is $\langle s \rangle$:

$$\langle s \rangle = +1\, P_{+1} + (-1)\, P_{-1}$$

$$= \frac{e^{-\beta E_+}}{q} - \frac{e^{-\beta E_-}}{q} \qquad q \equiv e^{-\beta E_+} + e^{-\beta E_-} = \text{"partition function"}$$

$$= \frac{e^{\beta\mu_0 B} - e^{-\beta\mu_0 B}}{e^{\beta\mu_0 B} + e^{-\beta\mu_0 B}} = \boxed{\tanh(\beta\mu_0 B)} =$$

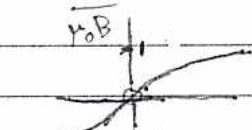


[Fig. 1]

How about ?:

$$\langle E \rangle = -\mu_0 B \frac{e^{-\beta E_+}}{q} + \mu_0 B \frac{e^{-\beta E_-}}{q} = -\mu_0 B \langle s \rangle = \boxed{-\mu_0 B \tanh(\beta\mu_0 B)}$$

So



[same as Fig. 1 !]

Note: $\langle E \rangle$ can be extracted directly from q: [I] $\boxed{\langle E \rangle = \frac{-\partial}{\partial\beta} \ln q}$ $= \frac{-\frac{\partial}{\partial\beta} q}{q} = \frac{-\frac{\partial}{\partial\beta}\left[e^{-\beta E_+} + e^{-\beta E_-}\right]}{q}$; $\left[e^{-\beta E_+} + e^{-\beta E_-}\right] \to 2\cosh(\beta\mu_0 B)$

$$= \frac{E_+ e^{-\beta E_+} + E_- e^{-\beta E_-}}{q} \checkmark$$

Note: Eq. [I] holds for any [N-~~level~~ state] system: Consider:

$$-\frac{\partial}{\partial\beta}\left[e^{-\beta E_1} + e^{-\beta E_2} + \cdots + e^{-\beta E_N}\right] = E_1 e^{-\beta E_1} + \cdots + E_N e^{-\beta E_N}$$

So [1] holds: $\langle E \rangle = \frac{1}{q}\left(E_1 e^{-\beta E_1} + \cdots + e^{-\beta E_N}\right)$ ✓

This suggests that we focus attention on calculating $\underline{\underline{q}}$ ← turns out to be a Holy Grail: all thermodynamic properties can be extracted from q.

[2] Calculate q for a 1-d harmonic oscillator: $\boxed{q} = \sum_{n=0}^{\infty} e^{-\beta\hbar\omega(n+\frac{1}{2})}$

$$= e^{-\beta\hbar\omega/2} \sum_{n=0}^{\infty} e^{-\beta\hbar\omega n} = \frac{e^{-\beta\hbar\omega/2}}{1-e^{-\beta\hbar\omega}} = \boxed{\frac{1}{2\sinh(\beta\hbar\omega/2)}}$$

$$\sum_{n=0}^{\infty} x^n = 1 + x + x^2 + \cdots = \frac{1}{1-x}$$

$x \equiv e^{-\beta\hbar\omega}$; $0 < x < 1$

low temperature,

(I) $T \to 0$

Study the limits [all systems are in $n=0$]

$$q = \frac{1}{e^{\beta\hbar\omega/2} - e^{-\beta\hbar\omega/2}} \xrightarrow[\beta\to\infty]{} e^{-\beta\hbar\omega/2} = \boxed{e^{-\beta E_0}} \checkmark$$

(II) $T \to \infty$

$$q \to \frac{1}{\beta\hbar\omega} = \boxed{\frac{kT}{\hbar\omega}}$$

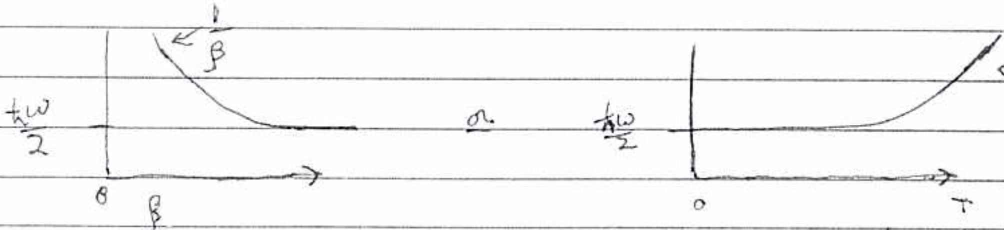
// also calculate:

$$\langle E \rangle = -\frac{\frac{\partial}{\partial\beta} q}{q} = \frac{-\frac{\partial}{\partial\beta}\frac{1}{\sinh(\beta\hbar\omega/2)}}{\frac{1}{\sinh(\beta\hbar\omega/2)}} = \frac{\hbar\omega}{2}\cdot\frac{\cosh(\beta\hbar\omega/2)}{\sinh(\beta\hbar\omega/2)} = \boxed{\frac{\hbar\omega}{2}\coth(\beta\hbar\omega/2)}$$

$\xrightarrow[\beta\to\infty]{} \hbar\omega/2$

$\xrightarrow[\beta\to 0]{} \frac{kT}{B}$

[consistent w/ classical equipartition thm ⇔ supports identification of $\beta \equiv 1/k_B T$]



* see below ↓

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One more example: p.f. for translational motion - 1-d particle in box [mass m, box size a]

$$q = \sum_{n=1}^{\infty} e^{-\beta h^2 n^2/8ma^2} \simeq \int_0^{\infty} dx\, e^{-\alpha x^2} \;;\quad \alpha \equiv \beta h^2/8ma^2$$

$$= \frac{1}{2}\sqrt{\frac{\pi}{\alpha}}$$

$$= \frac{1}{2}\sqrt{\frac{\pi \cdot 8ma^2}{\beta h^2}} = \boxed{a/\Lambda} \;;\quad \Lambda = \left[\frac{h^2}{2\pi m k_B T}\right]^{\frac{1}{2}}$$ = thermal de-Broglie wavelength.

for completeness, calculate

$$\langle E \rangle = -\frac{\partial q/\partial\beta}{q} = \frac{-\frac{\partial}{\partial\beta}\left(\frac{1}{\sqrt{\beta}}\right)}{\frac{1}{\sqrt{\beta}}} = \frac{1}{2\beta} = \boxed{\frac{k_B T}{2}}$$

✓ agrees w/ classical equipartition theorem.

Classical Equipartition Theorem ← Atkins [Ed. 8], Chapt. 2.

Given a molecule
(any molecule) at thermal equilibrium with a heat bath at absolute temperature T;
then as $T \to \infty$ (the high temp. limit):

Kinetic Energy:

$$\left\langle \tfrac{1}{2} m_\alpha v_{\alpha,i}^2 \right\rangle = \tfrac{1}{2} k_B T$$

for every Cartesian degree of freedom of every atom.

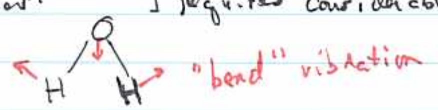
atom α ; $i = x, y, z$

Potential Energy:

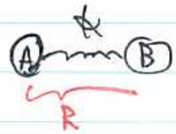
$$\langle (\text{vibrational potential energy})_j \rangle = \tfrac{1}{2} k_B T$$

for every vibrational (normal)* mode j

j^{th} vibrational mode

(*) NB: a precise definition of "normal mode of vibration"* for a polyatomic molecule [e.g., water: ] requires considerable work (!)

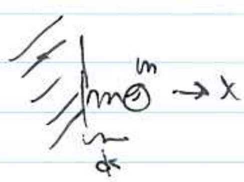
However, for a diatomic molecule:



$$\left\langle \tfrac{1}{2} k (R - R_e)^2 \right\rangle = \frac{k_B T}{2}$$

equilibrium bond length.

+ thus:



$$\left\langle \tfrac{1}{2} k x^2 \right\rangle = \frac{k_B T}{2}$$

x = displacement from equilibrium

let $m_A \to \infty$
$m_B \to m$

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(1)

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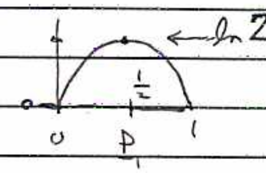
Gibbs Entropy formula

Statistical entropy: $\boxed{S = -k_B \sum_{k \, \text{states}} P_k \ln P_k}$

[e.g., for 2 states $\frac{S}{k_B} = -(P_1 \ln P_1 + P_2 \ln P_2)$, $P_2 = 1 - P_1$

$=$ ]

$$= -k_B \sum_k \frac{e^{-\beta E_k}}{q} \ln\left(e^{-\beta E_k}/q\right)$$

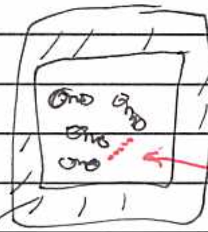
$$= -k_B \left\{ -\beta \sum_k \frac{E_k e^{-\beta E_k}}{q} - \ln q \cdot \underbrace{\cancel{\frac{\sum_k e^{-\beta E_k}}{q}}}_{1} \right\}$$

$$= \boxed{\frac{1}{T}\langle E \rangle + k_B \ln q}$$

finally:

$$A = \bar{E} - TS = \cancel{\bar{E}} - T\left\{ \frac{1}{T}\cancel{\bar{E}} + k_B \ln q \right\} = \boxed{-k_B T \ln q}$$

Generalize (notation) to a general interacting multiparticle system:



may be interactions between molecules.

T

canonical partition function

energy levels of the many-particle system

$$Q = \sum_j e^{-\beta E_j}$$

$$A = -k_B T \ln Q \; ; \quad \bar{E} = U = -\frac{\partial}{\partial \beta} \ln Q \; ; \quad S = k_B \ln Q + \bar{E}/T \quad (*)$$

can extract all thermo from here.