Central problem: How to calculate macroscopic, time-averaged properties from rapidly fluctuating microscopic quantities?

Brute force approach: Time-average over the microscopic properties

f_{obs} ≡ observed macroscopic property – pressure, etc.

$f\left(\underset{\sim}{\mathbf{q}}^{3N},\underset{\sim}{\mathbf{p}}^{3N}\right)$ ≡ microscopic mechanical variable

$$f_{obs} = \lim_{\tau\to\infty}\frac{1}{\tau}\int_0^{\tau} f\left(\underset{\sim}{\mathbf{q}}^{3N},\underset{\sim}{\mathbf{p}}^{3N}\right)d\tau' \quad \text{Time average}$$

But this requires calculation of time-dependent trajectories for all *N* particles!

Better approach: ENSEMBLE THEORY

Developed by J. Willard Gibbs – founder of statistical mechanics

Replaces time average with ensemble average

Ensemble ≡ collection of all possible states of an assembly

e.g. assembly of only *2 particles* quantum description

Constant energy ensemble with *7 quanta* of translational energy

State	n_{1x}	n_{1y}	n_{1z}	n_{2x}	n_{2y}	n_{2z}
α	2	1	1	1	1	1
β	1	2	1	1	1	1
γ	1	1	2	1	1	1
δ	1	1	1	2	1	1
ε	1	1	1	1	2	1
η	1	1	1	1	1	2

These are all of the 7-quanta states

$$E_\alpha = \sum_{i=1}^{N=2}\varepsilon_i$$

$$\varepsilon_i = \frac{h^2}{8ma^2}\left(n_{ix}^2+n_{iy}^2+n_{iz}^2\right) = \frac{h^2}{8ma^2}(3 \text{ or } 6)$$

classical description specify all the position & momentum variables

$$\begin{matrix} p_{1x} & p_{1y} & p_{1z} & p_{2x} & p_{2y} & p_{2z} \\ q_{1x} & q_{1y} & q_{1z} & q_{2x} & q_{2y} & q_{2z} \end{matrix}$$

$$E_\alpha = \sum_{i=1}^{N=2}\varepsilon_i \qquad \varepsilon_i = \left(p_{ix}^2+p_{iy}^2+p_{iz}^2\right)\big/2m$$

The *p* values squared must add to give the correct total energy.

QM ensemble average is a sum over states
CM ensemble average is an integral over states

ERGODIC HYPOTHESIS: Time average ⇔ Ensemble average

Ensemble average for macroscopic property *f*

$\overline{f} = \sum_j P_j f_j \quad P_j \equiv$ probability that assembly is in distinguishable assembly state j

$\sum_j P_j = 1$ probabilities are normalized

e.g. ensemble average energy: $\overline{E} = \sum_j P_j E_j$ note E_j are assembly energies

Ensemble average for continuous variables – classical treatment

$$\overline{f} = \int \cdots \int d\underline{\mathbf{q}}^{3N} d\underline{\mathbf{p}}^{3N} P\left(\underline{\mathbf{q}}^{3N}, \underline{\mathbf{p}}^{3N}\right) f\left(\underline{\mathbf{q}}^{3N}, \underline{\mathbf{p}}^{3N}\right)$$

where $P\left(\underline{\mathbf{q}}^{3N}, \underline{\mathbf{p}}^{3N}\right) d\underline{\mathbf{q}}^{3N} d\underline{\mathbf{p}}^{3N} \equiv$ probability of assembly being in volume element $d\underline{\mathbf{q}}^{3N} d\underline{\mathbf{p}}^{3N}$ centered at $\left(\underline{\mathbf{q}}^{3N}, \underline{\mathbf{p}}^{3N}\right)$

In either QM or CM case, we need a complete list of all the *distinguishable* assembly states and their probabilities P_j. How do we determine P_j?

They must give the minimum free energy under the experimental conditions!
e.g. minimum Helmholtz free energy *A* if we have fixed (*N, V, T*)

CANONICAL ENSEMBLE ≡ subject to constraint of constant (*N, V, T*)

- closed, thermodynamically stable system

The states of the assembly, given by $\{P_j\}$, must minimize *A*.

We need to write *A* in terms of the P_j values. How?

$$A = E - TS \qquad \overline{E} = \sum_j P_j E_j \quad \Rightarrow \quad A = \sum_j P_j E_j - TS$$

What about entropy *S*? The connection between *S* and {P_j} is *assumed* to be……

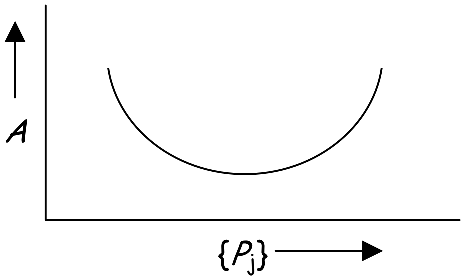
$$\boxed{S = -k\sum_j P_j \ln P_j}$$

Central assumption of Boltzmann (originally in somewhat different form that we'll see shortly). No derivation – only plausibility arguments. Statistical mechanics is built on this assumption!

$k = R/N_A = 1.38x10^{-23}$ J/K ≡ Boltzmann constant

$$A = E - TS = \sum_j P_j E_j + kT\sum_j P_j \ln P_j = \sum_j P_j\left(E_j + kT\ln P_j\right)$$

To find the {P_j} values that minimize *A*, imagine the real assembly at equilibrium, with the minimum *A* and the probabilities {P_j}, and other assemblies with non-equilibrium *A* and different {P_j} values.



Let {P_j} → {$P_j + \delta P_j$}

Then $A \to A + \delta A$

Find {δP_j} such that $\delta A = 0$

$$\delta A = \delta\left[\sum_j P_j\left(E_j + kT\ln P_j\right)\right] = \sum_j\left(E_j\delta P_j\right) + kT\ln P_j\delta P_j + kTP_j\frac{1}{P_j}\delta P_j = 0$$

$$\sum_j \delta P_j\left[E_j + kT\left(\ln P_j + 1\right)\right] = 0$$

Introduce constraint $\sum_j P_j = 1$

After $P_j \to P_j + \delta P_j$ still $\sum_j\left(P_j + \delta P_j\right) = 1$

Probabilities still add to 1 before or after the change {δP_j}.

Then $\sum_j \delta P_j = 0 \quad \Rightarrow \quad \delta P_1 = -\sum_{j=2}^{N} \delta P_j$

$$\delta A = \delta P_1\left[E_1 + kT\left(\ln P_1 + 1\right)\right] + \sum_{j=2}^{N}\delta P_j\left[E_j + kT\left(\ln P_j + 1\right)\right] = 0$$

$$\delta A = \sum_{j=2}^{N}\delta P_j\left[\left(E_j - E_1\right) + kT\left(\ln P_j - \ln P_1\right)\right] = 0$$

The δP_j's from j = 2 to *N* are completely independent, for arbitrary $\{\delta P_j\}$, so

$$\left(E_j - E_1\right) + kT\left(\ln P_j - \ln P_1\right) = 0 \quad \Rightarrow \quad \frac{P_j}{P_1} = \frac{e^{-E_j/kT}}{e^{-E_1/kT}}$$

$$P_j = P_1 e^{E_1/kT} e^{-E_j/kT} \qquad \sum_j P_j = 1 = P_1 e^{E_1/kT} \sum_j e^{-E_j/kT}$$

$$P_1 = \frac{e^{-E_1/kT}}{\sum_j e^{-E_j/kT}} \quad \text{same for } P_2, P_3, \ldots, P_n, \text{ any } P_j$$

$$\boxed{P_n = \frac{e^{-E_n/kT}}{\sum_j e^{-E_j/kT}} \quad \text{or} \quad P_j = \frac{e^{-E_j/kT}}{\sum_j e^{-E_j/kT}}}$$

<u>Canonical Distribution Function</u> gives the probability for the jth distinguishable state in the ensemble. This distribution minimizes *A* ⇒ *equilibrium distribution.*

We needed the key assumption $S = -k\sum_j P_j \ln P_j$

This leads to the result that <u>P_j depends on E_j only</u>

- ⇒ equal energy states have equal probabilities (seems highly plausible)
- ⇒ probability decreases exponentially w/ energy (familiar dependence)
- ⇒ probability of high-energy state increases with *T* (also familiar)

Denominator has special name…..**CANONICAL PARTITION FUNCTION *Q***

$$Q(N,V,T) = \sum_j e^{-E_j/kT}$$

Sum of "Boltzmann factors" $e^{-E_j/kT}$ over all the assembly states
Originally called "Zustandsumme" ≡ *Z* ≡ "sum over states"

Q is a <u>very</u> important quantity! So let's rewrite P_j in terms of it:

$$P_j = \frac{e^{-E_j/kT}}{\sum_j e^{-E_j/kT}} = \frac{e^{-E_j/kT}}{Q}$$

We'll be able to use *Q*, instead of any individual P_j values, to calculate everything! e.g. calculation of energy $\overline{E}$:

$$\overline{E} = \sum_j P_j E_j = f(Q)$$

Define $\beta = 1/kT$ so differentiation is simpler

$$Q(N,V,T) = \sum_j e^{-E_j/kT} = \sum_j e^{-\beta E_j} \qquad \frac{\partial Q}{\partial \beta} = -\sum_j E_j e^{-\beta E_j}$$

Recall $P_j = \dfrac{e^{-E_j/kT}}{Q}$ so $e^{-\beta E_j} = QP_j \;\Rightarrow\; \dfrac{\partial Q}{\partial \beta} = -\sum_j P_j E_j Q = -Q\sum_j P_j E_j = -Q\overline{E}$

$$\overline{E} = -\frac{1}{Q}\frac{\partial Q}{\partial \beta} = -\frac{\partial \ln Q}{\partial \beta} = -\frac{\partial \ln Q}{\partial (1/kT)} \qquad \boxed{\overline{E} = kT^2 \frac{\partial \ln Q}{\partial T}}$$

Ensemble average energy $\overline{E}$ in terms of *Q*, not P_j.

How about entropy?

$$S = -k\sum_j P_j \ln P_j = -k\sum_j P_j \ln\left(\frac{e^{-E_j/kT}}{Q}\right) = -k\sum_j P_j\left(-\frac{E_j}{kT} - \ln Q\right) = \frac{\sum_j P_j E_j}{T} + k\ln Q$$

$$\boxed{S = k\ln Q + \frac{\overline{E}}{T} = k\ln Q + kT\left(\frac{\partial \ln Q}{\partial T}\right)_{N,V}}$$

<u>Writing all thermodynamic functions or macroscopic properties in terms of *Q*</u>

From thermodynamics….. Helmholtz free energy $A = E - TS = E - kT\ln Q - T\dfrac{E}{T}$

$$\boxed{A = -kT\ln Q}$$

Monumentally important result!

From thermodynamics, $dA = -pdV - SdT + \mu dN$ (single component system) pressure $p = -\left(\frac{\partial A}{\partial V}\right)_{T,N}$ $\boxed{p = kT\left(\frac{\partial \ln Q}{\partial V}\right)_{T,N}}$

chemical potential $\mu = \left(\frac{\partial A}{\partial N}\right)_{T,V}$ $\boxed{\mu = -kT\left(\frac{\partial \ln Q}{\partial N}\right)_{T,V}}$

$$\left.\begin{array}{l} H = E + pV \\ G = A + pV \end{array}\right\} \begin{array}{l} \text{Homework:} \\ \text{Write in terms of } Q \end{array}$$

Now we have a framework for relating microscopic properties, as given by *Q*, to macroscopic properties.
Note that $Q(E_j)$ or $P_j(E_j)$ tells us the distribution of assembly states in the ensemble. <u>Only the energy</u> of an assembly state determines its probability. *Q* and P_j don't depend on any other properties of the states.

<u>Alternate form for the probabilities</u>
Sometimes, more useful than P_j – probability of distinguishable state j – is $P(E)$, probability of finding an assembly with <u>energy *E*</u>.

Recall $Q(N,V,T) = \sum_j e^{-E_j/kT} = \cdots + e^{-E_\alpha/kT} + e^{-E_\beta/kT} + \cdots$

But many distinguishable states are <u>degenerate</u>, e.g. $E_\alpha = E_\beta = E_\gamma \equiv E$

then $Q(N,V,T) = \cdots + 3e^{-E/kT} + \cdots = \sum_E \Omega(N,V,E)e^{-E/kT}$

$\Omega(N,V,E)$ ≡ degeneracy ≡ # distinguishable assembly states with energy *E*

$$Q(N,V,T) = \sum_j e^{-E_j/kT} = \sum_E \Omega(N,V,E)e^{-E/kT}$$

sum over assembly states

sum over assembly energy levels

$$P(E) = \sum_{j \ni \{E_j = E\}} P_j = \sum_{j \ni \{E_j = E\}} e^{-E_j/kT} \Big/ Q(N,V,T)$$

sum over those assembly states with $E_j = E$

$$\boxed{P(E) = \frac{\Omega(N,V,E)e^{-E/kT}}{Q(N,V,T)}}$$