Understanding Molecular Simulation

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Why Simulation?

1. **Predicting properties of (new) materials**
2. **Understanding phenomena on a molecular scale.**
3. ~~**Reproducing known phenomena.**~~

Testing simulations by:

Reproducing known phenomena.

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THE question:

"Can we predict the macroscopic properties of (classical) many-body systems?"

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…. There are so many molecules.

This is why, before the advent of the computer, it was impossible to predict the properties of real materials.

What was the alternative?

1. Smart tricks ("theory")

   Only works in special cases

2. Constructing model ("molecular lego")…

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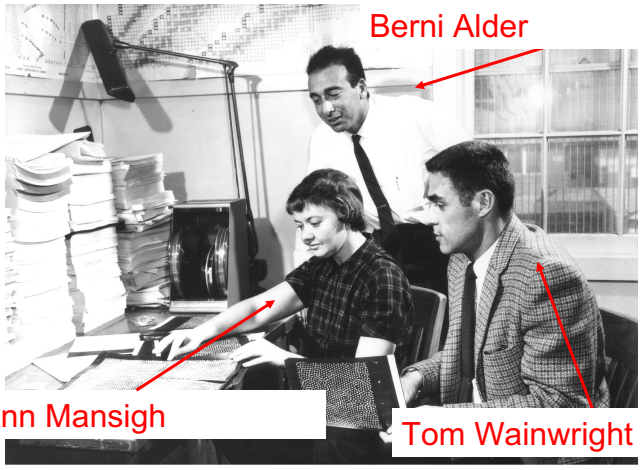
The computer age (1953…)



With computers we can follow the behavior of hundreds to hundreds of millions of molecules.

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What properties do we wish to predict?

The positions and velocities of all molecules? **No.**

We are interested in properties that can be measured.

These are typically, **averaged** properties:

Pressure, temperature, heat capacity, magnetic susceptibility, etc…

http://physics.weber.edu/schroeder/software/demos/MDv0.html

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Thermodynamics and Statistical Mechanics:

The languages of Molecular Simulation

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Language: **Thermodynamics**

Very brief review of Thermodynamics

3 Laws:

$dE = q + w$ First Law

In a closed system,
Heat cannot flow from
"cold" to "hot"

Second Law

$S(T = 0) = 0$ Third Law

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+ “0-th” law:

If body A is in equilibrium with body B
and body B is in equilibrium with body C
then A is in equilibrium with C

Fourth law?

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NERNST’s argument why there cannot be a Fourth Law of Thermodynamics.

Number of people involved	Names	Law
3	Mayer Joule Helmholtz	First law
2	Carnot Clausius	Second law
1	Nernst	Third Law
0	--	Fourth Law ?

Therefore, there cannot be a Fourth Law of Thermodynamics !

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Thermodynamics provides phenomenological RELATIONS between macroscopic observables.

Thermodynamics does not PREDICT observables.

In fact, thermodynamics “knows” nothing about atoms, molecules, quantum mechanics etc:

it is just as valid now as it was in the 19th century.

In order to <u>predict</u> the equilibrium properties of many-body systems, we need Statistical Mechanics.

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To “derive” the basic relations of Statistical Mechanics, we use a quantum picture - then we go to a classical description.

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Central assumption: the “Ergodic” hypothesis.

A system of **N** particles in volume **V** and with energy **E**, has $\Omega(E)$ energy eigenstates.

Ergodic hypothesis: “***Every eigenstate at constant N,V,E is equally likely to be occupied”.***

$\Rightarrow$ *all of equilibrium statistical mechanics*.

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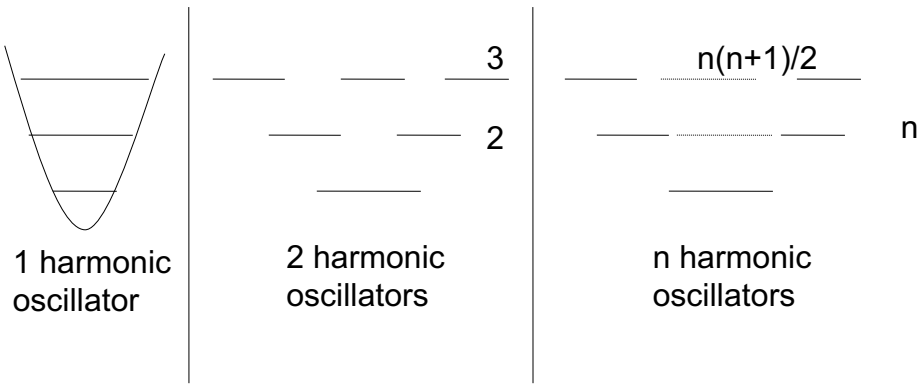
For macroscopic systems, $\Omega(E)$ is a “super-astronomically large” number



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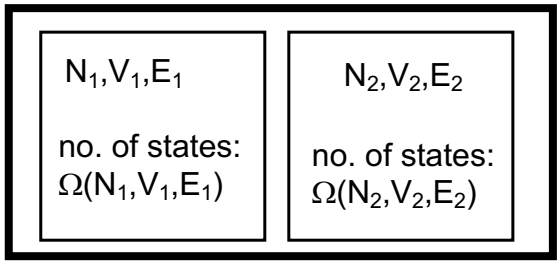
Now consider two systems with total energy **E**.



$$\Omega(E_1, E_2) = \Omega_1(N_1, V_1, E_1) \times \Omega_2(N_2, V_2, E_2)$$
$$= \Omega_1(E_1, V_1, N_1) \times \Omega_2(E - E_1, V_2, N_2)$$

This function of E_1 is **very** sharply peaked (for macroscopic systems)

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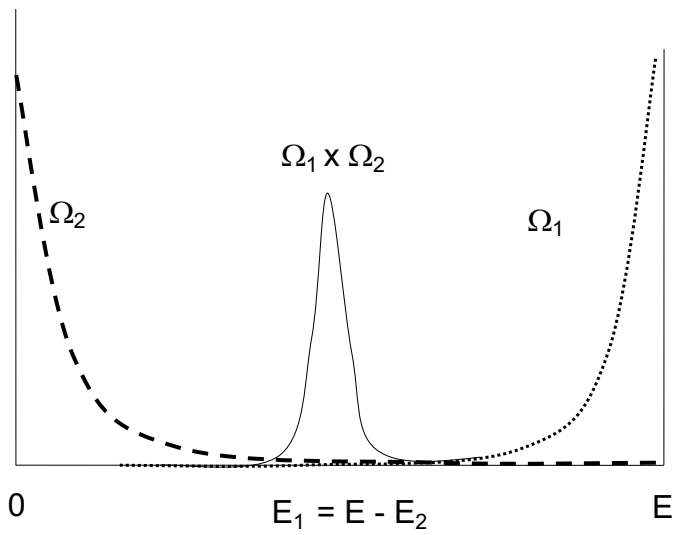

For macroscopic systems, $\Omega_1 \times \Omega_2$ has a sharp maximum

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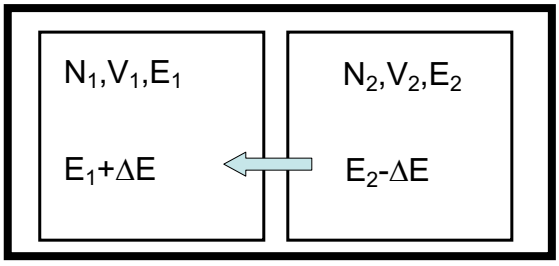

Now, allow energy exchange between **1** and **2.**

The most likely energy distribution is the one that maximizes $\Omega_1 \times \Omega_2$.

It is more convenient (but equivalent) to maximize $\ln(\Omega_1 \times \Omega_2)$.

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So:

$$\left(\frac{\partial \ln \Omega(E_1, E - E_1)}{\partial E_1}\right)_{N,V,E} = 0$$

With:

$$\ln \Omega(E_1, E - E_1) = \ln \Omega_1(E_1) + \ln \Omega_2(E - E_1)$$

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$$\left(\frac{\partial \ln \Omega_1(E_1)}{\partial E_1}\right)_{N_1,V_1} + \left(\frac{\partial \ln \Omega_2(E_2)}{\partial E_1}\right)_{N_2,V_2} = 0$$

but $\mathrm{d}E_2 = -\mathrm{d}E_1$, hence:

$$\left(\frac{\partial \ln \Omega_1(E_1)}{\partial E_1}\right)_{N_1,V_1} = \left(\frac{\partial \ln \Omega_2(E_2)}{\partial E_2}\right)_{N_2,V_2}$$

This is the condition for thermal equilibrium ("no spontaneous heat flow between 1 and 2")

In thermodynamics, thermal equilibrium means: equal temperatures…

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Let us define:

$$\beta(E,V,N) \equiv \left(\frac{\partial \ln \Omega(E,V,N)}{\partial E}\right)_{N,V}$$

Then, thermal equilibrium is equivalent to:

$$\beta(E_1,V_1,N_1) = \beta(E_2,V_2,N_2)$$

This suggests that β is a function of T.

Relation to classical thermodynamics:

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We know that, in equilibrium,
$\ln \Omega$ is a a maximum.

Conjecture: $\ln \Omega = S$

Almost right.

Good features:

•Extensivity

•Third law of thermodynamics comes for free

Bad feature:

•It assumes that entropy is dimensionless but
(for unfortunate, historical reasons, it is not…)

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We have to live with the past, therefore:

$$S = k_B \ln \Omega$$, with k_B= 1.380662 10^{-23} J/K

In thermodynamics, the absolute (Kelvin) temperature scale was defined such that:

$$\left(\frac{\partial S}{\partial E}\right)_{N,V} = \frac{1}{T}$$ (recall: dE=TdS-PdV+μdN)

But we found (defined):

$$\beta(E,V,N) \equiv \left(\frac{\partial \ln \Omega(E,V,N)}{\partial E}\right)_{N,V}$$

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This gives the "statistical" definition of temperature:

$$\frac{1}{T} = k_B \left(\frac{\partial \ln \Omega(E, V, N)}{\partial E} \right)_{N,V}$$

In short:

Entropy and temperature are both related to the fact that we can COUNT states.

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How large is Ω?

For macroscopic systems, **super-astronomically** large.

For instance, for a glass of water at room temperature:

$$\Omega \approx 10^{2\ 10^{25}}$$

Macroscopic deviations from the second law of thermodynamics are not forbidden, but they are extremely unlikely.

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Deviations from the Second Law:

Suppose that the entropy of a glass of water decreases by 1 part in 10^9. This decreases the Ω by a factor R:

$$R = \frac{\Omega'}{\Omega} = e^{(S'-S)/k_B} \approx 10^{-2\,10^{-9}10^{25}} = 10^{-2\,10^{16}} \approx 0$$

Macroscopic deviations from the second law of thermodynamics are not forbidden, but they are extremely unlikely.

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A mathematical relation:
$10^{-10^{16}} \neq 0$

A physical relation:
$10^{-10^{16}} \approx 0$

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Deriving the Boltzmann distribution

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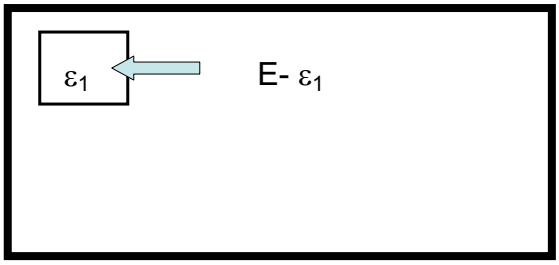

Consider a "small" system (a molecule, a virus, a mountain) in thermal contact with a much larger system ("bath").

The total energy is fixed. The higher the energy of the small system, the lower the energy of the bath.

What happens to the total number of accessible states?

The small system is in a single, specific state.

The bath can be in Ω_B states.

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$$\ln \Omega_B(E-\epsilon_i) = \ln \Omega_B(E) - \epsilon_i \frac{\partial \ln \Omega_B(E)}{\partial E} + \mathcal{O}(1/E)$$

But, as β=1/k_BT :

$$\ln \Omega_B(E-\epsilon_i) = \ln \Omega_B(E) - \epsilon_i/k_BT + \mathcal{O}(1/E)$$

The probability that the small system is in a **given** ("labelled") state with energy ε_i is

$$P(\epsilon_i) = \frac{1 \times \Omega_B(E-\epsilon_i)}{\sum_i \Omega_B(E-\epsilon_i)}$$

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using

$$\Omega_B(E-\epsilon_i) = \Omega_B(E)\exp(-\epsilon_i/k_BT)$$

we get

$$P(\epsilon_i) = \frac{\Omega_B(E)\exp(-\epsilon_i/k_BT)}{\sum_i \Omega_B(E)\exp(-\epsilon_i/k_BT)} = \frac{\exp(-\epsilon_i/k_BT)}{\sum_i \exp(-\epsilon_i/k_BT)}$$

This is the Boltzmann distribution:

"Low energies are more likely than high energies"

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Why can we ignore higher-order terms in the Taylor expansion?

$$\ln \Omega_B(E-\epsilon_i) = \ln \Omega_B(E) - \epsilon_i \frac{\partial \ln \Omega_B(E)}{\partial E} + \frac{\epsilon_i^2}{2}\frac{\partial^2 \ln \Omega_B(E)}{\partial E^2} + \cdots$$

Look at the third term on the right:

$$\frac{\epsilon_i^2}{2}\frac{\partial^2 \ln \Omega_B(E)}{\partial E^2} = \frac{\epsilon_i^2}{2}\frac{\partial \beta(E)}{\partial E} = -\frac{\epsilon_i^2}{2k_B T^2 C_V(\text{bath})}$$

This term, and all higher-order, vanish as the heat capacity of the bath $\Rightarrow \infty$ in the thermodynamic limit.

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The probability to find the system in state *i* is:

$$p_i = \frac{\exp(-\beta\epsilon_i)}{Q}$$

$$\beta \equiv 1/k_B T$$

Where we have defined the partition sum Q:

$$\boxed{Q \equiv \sum_i e^{-\beta\epsilon_i}}$$

End lecture 1

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Brief Summary:

1. System at constant N,V & E has a large but finite number of states: Ω(N,V,E)
2. "Every eigenstate at constant N,V,E is equally likely to be occupied"
3. Postulate relation between Ω and entropy:

   $S = k_B \ln \Omega(N, V, E)$
4. Boltzmann distribution: $$P(\epsilon_i) = \frac{e^{-\beta\epsilon_i}}{\sum_j e^{-\beta\epsilon_j}}$$

$$\beta \equiv \frac{1}{k_B T}$$

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The average energy is

$$< E >= \sum_i p_i \epsilon_i = \sum_i \frac{\epsilon_i \exp(-\beta\epsilon_i)}{Q}$$

$$= -\frac{\frac{\partial}{\partial\beta}\sum_i e^{-\beta\epsilon_i}}{Q} = -\frac{\frac{\partial}{\partial\beta}Q}{Q} = -\frac{\partial \ln Q}{\partial\beta}$$

Notation:

$\langle \cdots \rangle$ = "thermal average".

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Therefore

$$< E >= -\frac{\partial \ln Q}{\partial \beta} = -\frac{\partial \ln Q}{\partial 1/k_B T}$$

This can be compared to the thermodynamic relation between the Helmholtz Free Energy **A** and the temprature **T**:

$$E = \left(\frac{\partial A/T}{\partial 1/T}\right) = \left(\frac{\partial A/k_B T}{\partial 1/k_B T}\right)$$

(dA=-SdT-PdV+μdN)

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This suggests that the partition sum

$$Q = \sum_i \exp(-\beta \epsilon_i)$$

is related to the Helmholtz free energy A through:

$$A = -k_B T \ln Q + \cancel{\text{constant}}$$

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Expression for heat capacity C_V.

Recall:

$$A = -k_B T \ln Q$$

with

$$Q = \sum_i \exp(-\beta \epsilon_i)$$

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Then the heat capacity is

$$C_V = \frac{\partial E}{\partial T} = \left(\frac{\partial E}{\partial \beta}\right)\left(\frac{\partial \beta}{\partial T}\right) = -\frac{1}{k_B T^2}\frac{\partial E}{\partial \beta}$$

Using our expression for **E:**

$$C_V = -\frac{1}{k_B T^2}\frac{\partial}{\partial \beta}\sum_i \frac{\epsilon_i \exp(-\beta \epsilon_i)}{Q}$$

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Both the numerator and denominator depend on β.

$$C_V = +\frac{1}{k_B T^2}\left(\sum_i \frac{\epsilon_i^2 \exp(-\beta\epsilon_i)}{Q} - \left[\sum_i \frac{\epsilon_i \exp(-\beta\epsilon_i)}{Q}\right]^2\right)$$

And, finally:

$$C_V = \frac{1}{k_B T^2}\left(< E^2 > - < E >^2\right)$$

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$$C_V = \frac{1}{k_B T^2}\left(< E^2 > - < E >^2\right)$$

Consequences:

1. Heat capacity is always ≥ 0 (…)
2. We can estimate the fluctuations in the energy from our knowledge of the heat capacity.
   Example: Ideal monatomic gas.

$$\frac{\sigma_E}{E} = \frac{\sqrt{< E^2 > - < E >^2}}{E} = \sqrt{\frac{k_B T^2 C_V}{E^2}}$$

But: E = 1.5 Nk_BT and C_V=1.5 Nk_B. Therefore:

$$\frac{\sigma_E}{E} = \sqrt{\frac{1.5 N k_B^2 T^2}{(1.5 N k_B T)^2}} = \frac{1}{\sqrt{1.5N}}$$ (order 10^{-12} for 1 mol)

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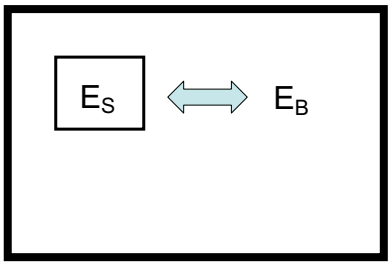

Second law of thermodynamics:

S is maximum in closed system.

$$S_{\text{total}} = S_{\text{bath}} + S_{\text{system}}$$

$$k_B \ln \Omega_{tot} = k_B \ln \Omega_B(E_{tot} - E_s) + S_{\text{system}}$$

$$= k_B \ln \Omega_B(E_{tot}) - k_B E_S \frac{\partial \ln \Omega_B}{\partial E_B} + S_{\text{system}}$$

$$= \text{number} - \frac{E_{\text{system}}}{T} + S_{\text{system}}$$

This must be at a maximum.

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Therefore:

$$\frac{E_{\text{system}}}{T} - S_{\text{system}} = \frac{A_{\text{system}}}{T}$$

must be at a minimum.

As T≥0, it follows that the Helmholtz free energy **A** at constant N,V,T is at a minimum.

Similar results can be derived for a system at constant N,P,T (**G** is minimal) or at constant μ,V,T (**P** is maximal).

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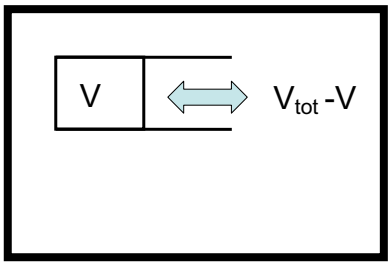
Constant pressure:



$$\ln \Omega(V, V_{tot} - V) = \ln \Omega_{sys}(V) + \ln \Omega_{\text{bath}}(V_{tot} - V)$$

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As $S = k_B \ln \Omega$

$$\left(\frac{\partial S_{sys}}{\partial V}\right)_{E,N} + \left(\frac{\partial S_{\text{bath}}}{\partial V}\right)_{E,N} = 0$$

Thermodynamics:

$$dS = \frac{dE}{T} + \frac{P}{T} dV - \frac{\mu}{T} dN$$

Hence:

$$\left(\frac{\partial S}{\partial V}\right)_{E,N} = \frac{P}{T}$$

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Conditions for equilibrium:

$$T_{sys} = T_{\text{bath}}$$

and

$$P_{sys} = P_{\text{bath}}$$

More convenient:

$$dA = -PdV - SdT + \mu dN$$

Pressure:

$$P = -\left(\frac{\partial A}{\partial V}\right)_{T,N}$$

Hence:

$$P = k_B T \left(\frac{\partial \ln Q}{\partial V}\right)_{T,N}$$

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Now: from quantum picture to classical description.

We have assumed quantum mechanics (discrete states) but
In practice we are often interested in the classical limit

$$\sum_i e^{-\beta E_i} \to \frac{1}{h^{3N} N!} \int \int d\mathbf{p}^N \, d\mathbf{r}^N \, e^{-\beta \left[\sum_i \frac{p_i^2}{2m_i} + U(\mathbf{r}^N)\right]}$$

Why? Show ?

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Hand-waving argument (it can be done better):

Uncertainty relation: $\Delta x \times \Delta p = \mathcal{O}(h)$

$$\sum_{states} (\cdots) \rightarrow \frac{1}{h} \int_0^L dx \int_{p_{min}}^{p_{max}} dp_x (\cdots)$$

Interpretation: every quantum state of a 1-dimensional system occupies a "volume" ***h*** in the "phase space" of coordinates and momenta.

For N particles in 3D: volume of quantum state is h^{3N}.

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We now replace the quantum partition *sum* by the classical partition *function*.

$$\sum_i e^{-\beta E_i} \rightarrow \frac{1}{h^{3N} N!} \int \int d\mathbf{p}^N \, d\mathbf{r}^N \, e^{-\beta \left[\sum_i \frac{p_i^2}{2m_i} + U(\mathbf{r}^N) \right]}$$

N! is usually attributed to the fact that identical quantum particles are indistinguishable – but the relation is also meaningful for classical system (see later).

$$Q_{\text{classical}} = \frac{1}{h^{3N} N!} \int d\mathbf{r}^N d\mathbf{p}^N e^{-\beta \left[U(r^N) + K(p^N) \right]}$$

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Thermal averages:

$$\langle X \rangle = \frac{\sum_i e^{-\beta\epsilon_i} < i|X|i >}{\sum_i e^{-\beta\epsilon_i}}$$

Classical limit

$$\langle X \rangle_{cl} = \frac{\int d\mathbf{p}^N d\mathbf{r}^N e^{-\beta(K+U)} X(\mathbf{p}^N, \mathbf{r}^N)}{\int d\mathbf{p}^N d\mathbf{r}^N e^{-\beta(K+U)}}$$

$U(\mathbf{r}^N)$ Potential energy (depends on all particle coordinates)

$$K(\mathbf{p}^N) = \sum_{j=1}^{N} \frac{p_j^2}{2m_j}$$

Kinetic energy (depends on all particle momenta)

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$$Q_{\text{classical}} = \frac{1}{h^{3N} N!} \int dr^N dp^N e^{-\beta\left[U(r^N)+K(p^N)\right]}$$

Separate integration over positions and momenta:

$$\int dr^N dp^N e^{-\beta\left[U(r^N)+K(p^N)\right]} = \int dp^N e^{-\beta K(p^N)} \int dr^N e^{-\beta U(r^N)}$$

We can carry out the integration over momenta analytically:

$$\int dp^N e^{-\beta K(p^N)} = \left(\int dp e^{-\frac{p^2}{2mk_BT}}\right)^{3N} = (2\pi m k_B T)^{3N/2}$$

Therefore:

$$Q_{\text{classical}} = \frac{(2\pi m k_B T)^{3N/2}}{h^{3N} N!} \int dr^N e^{-\beta U(r^N)}$$

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We define *de Broglie* thermal wavelength Λ as:

$$\Lambda \equiv \left(\frac{h^2}{2\pi m k_B T}\right)^{\frac{1}{2}}$$

Then we can write:

$$Q_{\text{classical}} = \frac{1}{\Lambda^{3N} N!} \int dr^N e^{-\beta U(r^N)}$$

Now we can check if the assumption $S=k_B \ln \Omega$ is justified.

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Consider ideal (monatomic) gas.
We know (from experiment):

$PV=nRT$ and $C_V= 1.5\ nR$

Now we will compute Q and use $A=-k_B T \ln Q$:

$$Q = \frac{1}{\Lambda^{3N} N!} \int dr^N e^{-\beta U(r^N)} = \frac{V^N}{\Lambda^{3N} N!}$$

Pressure: $$P = -\left(\frac{\partial A}{\partial V}\right)_{N,T} = \frac{N}{\beta V} = \frac{N k_B T}{V}$$

and hence $Nk_BT=nR$, or $k_B=R/N_{Avogadro}= 1.380662\ 10^{-23}$ J/K

Energy: $$E = -\left(\frac{\partial A/T}{\partial 1/T}\right)_{N,T} = \frac{3N}{\Lambda}\frac{\partial \Lambda}{\partial \beta} = \frac{3}{2} N k_B T$$

And hence: $C_V=1.5\ Nk_B = 1.5\ nR$

End lecture 2

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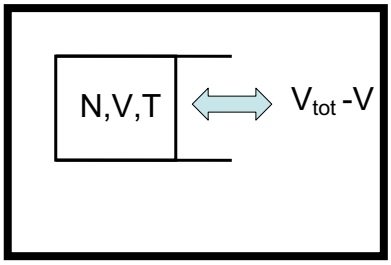

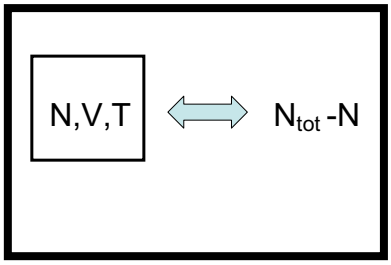

Constant pressure: system can exchange volume with a reservoir.

Constant chemical potential: system can exchange particles with a reservoir.

Fixed N,P & T

Fixed μ,V & T

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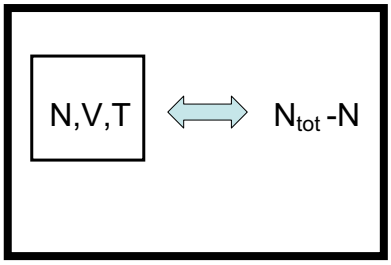

$$\ln \Omega_B(E_T - E_s, N_T - N_s) = \ln \Omega_B(E_T, N_T) - \frac{\partial \ln \Omega_B}{\partial E} E_s - \frac{\partial \ln \Omega_B}{\partial N} N_s$$

$$\ln \Omega_B(E_T - E_s, N_T - N_s) = \ln \Omega_B(E_T, N_T) - \frac{E_s}{k_B T} + \frac{\mu N_s}{k_B T}$$

Because from dE=TdS-PdV+μdN it follows that

$$\left(\frac{\partial S}{\partial N}\right)_{E,V} = -\frac{\mu}{T}$$

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$$P(\epsilon_i, N_i) = \frac{e^{-\beta\epsilon_i} e^{\beta\mu N_i}}{\sum_{j,N_j} e^{-\beta\epsilon_j} e^{\beta\mu N_j}}$$

$$P(\epsilon_i, N_i) = \frac{e^{-\beta\epsilon_i} e^{\beta\mu N_i}}{\sum_{N=0}^{\infty} Q(N,V,T) e^{\beta\mu N}}$$

$$\sum_{N=0}^{\infty} Q(N,V,T) e^{\beta\mu N} \equiv \Xi$$

"Ensembles":

Constant E,V,N: "micro-canonical ensemble"

Constant T,V,N: "canonical ensemble"

Constant μ,V,T: "Grand-canonical ensemble"

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PHASE COEXISTENCE

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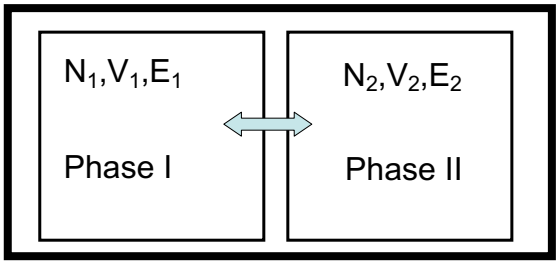
First, we derive the conditions for phase coexistence.



S is maximal. Therefore: $dS = dS_I + dS_{II} = 0$

$$dS_I = \frac{1}{T_I} dE_I + \frac{P_I}{T_I} dV_I - \frac{\mu_I}{T_I} dN_I$$

$$dS_{II} = \frac{1}{T_{II}} dE_{II} + \frac{P_{II}}{T_{II}} dV_{II} - \frac{\mu_{II}}{T_{II}} dN_{II}$$

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But: $dE_{II} = -dE_I$, $dV_{II}=-dV_I$ and $dN_{II}=- dN_I$
Therefore:

$$dS_{tot} = \left(\frac{1}{T_I} - \frac{1}{T_{II}}\right) dE_I + \left(\frac{P_I}{T_I} - \frac{P_{II}}{T_{II}}\right) dV_I - \left(\frac{\mu_I}{T_I} - \frac{\mu_{II}}{T_{II}}\right) dN_I$$

dS_{tot} must vanish for arbitrary dE_I, dV_I and dN_I. Hence:

Phase coexistence requires:

$T_I=T_{II}$

$P_I=P_{II}$

$\mu_I= \mu_{II}$

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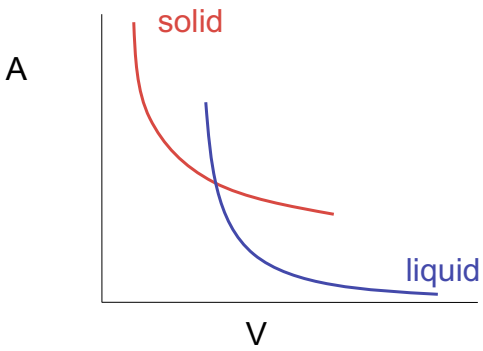
At constant temperature, the condition for equilibrium is that the Helmholtz free energy **A** is at a minimum.

Suppose that we know **A(N,V,T)** for two phases (say, solid and liquid)



Coexistence:
$P_I = P_{II}$
$\mu_I = \mu_{II}$

$$P = -\left(\frac{\partial A}{\partial V}\right)_{T,N}$$

So $P_I = P_{II}$ means: equal slopes

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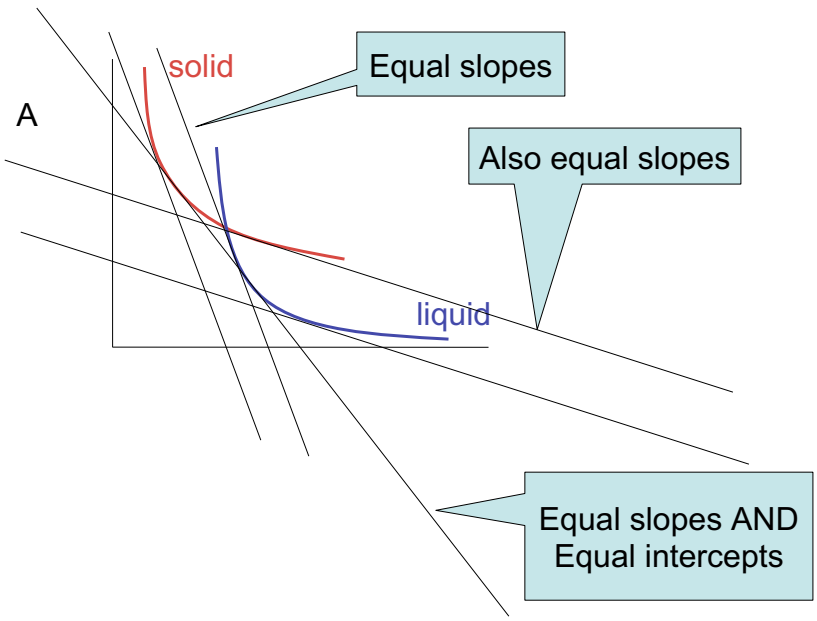

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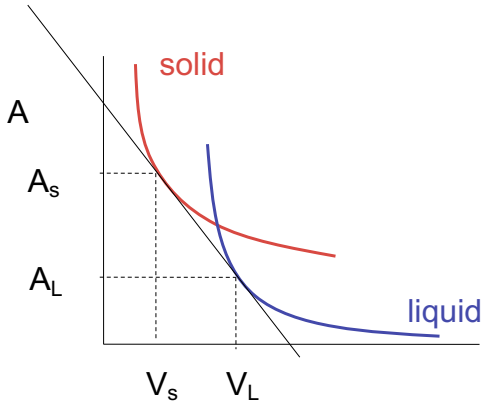

What is the meaning of equal intercepts?

E.g.: intercept of "solid" curve:

$$A_S - \left(\frac{\partial A_S}{\partial V}\right)_{N,T} V_S = A_S + P_S V_S = G_S = N\mu_S$$

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Similarly, for "liquid" curve:

$$A_L - \left(\frac{\partial A_L}{\partial V}\right)_{N,T} V_L = A_L + P_L V_L = G_L = N\mu_L$$

Therefore, if both the slopes and the intercepts are equal, we have:

$P_S = P_L$

$\mu_S = \mu_L$

And, as we work at constant temperature:
$T_S = T_L$

"Common tangent" construction locates point of phase coexistence.

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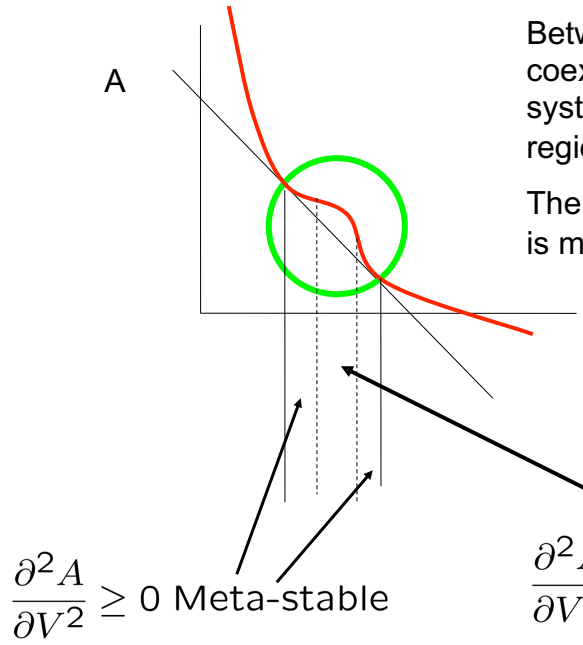

Between the two coexistence points, the system is in a two-phase region.

The homogeneous phase is meta-stable/unstable.

$$\frac{\partial^2 A}{\partial V^2} \geq 0 \text{ Meta-stable}$$

$$\frac{\partial^2 A}{\partial V^2} \leq 0 \text{ Unstable}$$

End lecture 4

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To locate phase coexistence, we need to know A as a function of V and T.

How?

In experiment: we cannot measure A directly.

But we can measure:

$$P = -\left(\frac{\partial A}{\partial V}\right)_{N,T}$$

and we can compute A exactly in certain limits

(e.g. ideal gas)

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Suppose that at a sufficiently large volume V_0, the system behaves as an ideal gas. Then: $A(V_0)=A_{id}(V_0)$ and:

$$A(V) = A_{id}(V_0) + \int_{V_0}^{V} dV' \left(\frac{\partial A}{\partial V'}\right)_{N,T}$$

$$A(V) = A_{id}(V_0) - \int_{V_0}^{V} dV' \, P(V')$$

known

Alternative: if we know A(N,V,T) at some temperature T_0 then:

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$$\frac{A(T)}{T} = \frac{A(T_0)}{T_0} + \int_{1/T_0}^{1/T} d\frac{1}{T'} \left(\frac{\partial A/T'}{\partial 1/T'}\right)_{N,V}$$

$$\frac{A(T)}{T} = \frac{A(T_0)}{T_0} + \int_{1/T_0}^{1/T} d\frac{1}{T'} \, E(N,V,T')$$

known

Why do we need this complicated route to locate coexistence?

Meta-stability (e.g. solid-solid) - phase transformation occurs only after super-cooling/super-heating.

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To predict phase transitions:

- We need to compute Q(N,V,T)
- From that we compute A(N,V,T)
- Then use double-tangent construction

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The limits of Simulation

Brute-force simulations can never bridge all the scales between microscopic (nanometers/picoseconds) and macroscopic (cells, humans, planets).

Hence: we need different levels of description ("coarse graining") - and we need input from experiments at many different levels to validate our models.

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The limits of Experiments

Increasingly, experiments generate far more data than humans can digest.

Result: "Experulation".

Simulations are becoming an integral part of the analysis of experimental data.

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[redacted]

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Where does the factor N! come from?

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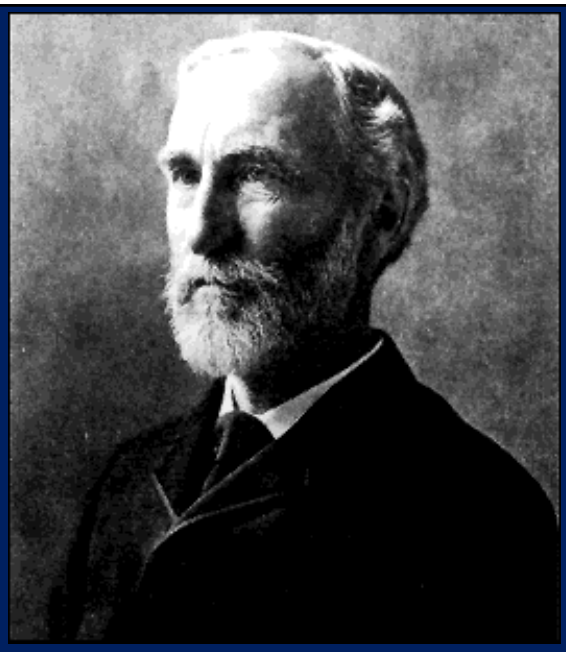

The Gibbs Paradox

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What do the textbooks say?

Thus, it seems that the $1/N!$ term is absolutely necessary to resolve the paradox. This means that only a correct quantum mechanical treatment of the ideal gas gives rise to a consistent entropy.

could only later be identified with Planck's constant h. The indistinguishability of particles of the same kind, which had to be introduced in order to avoid the *Gibbs' paradox*,[1] got a firm logical basis only after the invention of quantum theory. The observed distribution of black-body radiation could

least one nucleon mass). Hence the distinction between identical and non-identical molecules is completely unambiguous in a quantum-mechanical description. The Gibbs paradox thus foreshadowed already in the last century conceptual difficulties that were resolved satisfactorily only by the advent of quantum mechanics.

It is not possible to understand classically why we must divide $\sum(E)$ by N! to obtain the correct counting of states. The reason is inherently quantum mechanical. Quantum mechanically, atoms are inherently indistinguishable in the following sense: A state of the gas is described by an N-particle wave function, which is either symmetric or antisymmetric with respect to the interchange of any

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LANDAU & LIFSHITZ footnote

† This becomes particularly evident if we consider the classical partition function (integral over states) as the limit of the quantum partition function. In the latter the summation is over all the different quantum states, and there is no problem (remembering that, because of the principle of symmetry of wave functions in quantum mechanics, the quantum state is unaffected by interchanges of identical particles).

From the purely classical viewpoint the need for this interpretation of the statistical integration arises because otherwise the statistical weight would no longer be multiplicative, and so the entropy and the other thermodynamic quantities would no longer be additive.

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Van Kampen

In *statistical mechanics* this dependence is obtained by inserting a factor $1/N!$ in the partition function. Quantum mechanically this factor enters automatically and in many textbooks that is the way in which it is justified. My point is that this is irrelevant: *even in classical statistical mechanics it can be derived by logic* — rather than by the somewhat mystical arguments of Gibbs[2] and Planck.[3,4] Specifically I take exception to such statements as: "It is not possible to understand classically why we must divide by $N!$ to obtain the correct counting of states",[5] and: "Classical statistics thus leads to a contradiction with experience even in the range in which quantum effects in the proper sense can be completely neglected".[6]

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ENTER JAYNES:

"Usually, Gibbs' prose style conveys his meaning in a sufficiently clear way…"

"… using no more than twice as many words as Poincaré or Einstein would have used to say the same thing"

"But occasionally he delivers a sentence with a ponderous unintelligibility that seems to challenge us to make sense out of it…"

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GIBBS's SENTENCE:

"Again, when such gases have been mixed, there is no more impossibility of the separation of the two kinds of molecules in virtue of their ordinary motion in the gaseous mass without any especial external influence, than there is of the separation of a homogeneous gas into the same two parts into which it has once been divided, after these have these have once been mixed"

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Treat as gas of N particle that are all very similar, so that we cannot separate them, then

$$Z_{dist}(N) = V^N$$ (ln Z_{dist} is not extensive)

Now: two such systems with N_1 and N_2 particles. In equilibrium, we can distribute the particles over the two systems in any way we choose (with fixed N_1 and N_2).

$$Z_{combined}(N_1, V_1, N_2, V_2) = V_1^{N_1} V_2^{N_2} \times \frac{(N_1 + N_2)!}{N_1! N_2!}$$

ln $Z_{combined}$ is **not** extensive. Not even in quantum mechanics.

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When the two systems are in equilibrium, the partition function is maximal with respect to variations in N_1 (dN_1=-dN_2).

$$\left(\frac{\partial \ln Z_c}{\partial N_1}\right)_N = \frac{\partial \ln Z_1/N_1!}{\partial N_1} - \frac{\partial \ln Z_2/N_2!}{\partial N_2} = 0$$

Therefore, as soon as we are computing the **chemical potential**, we MUST include the factor N!, also for labeled/classical particles.

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Conveniently, the partition function of the combined system then factorizes

$$\frac{Z_c(N_1, V_1, N_2, V_2)}{(N_1 + N_2)!} = \frac{Z_1}{N_1!}\frac{Z_2}{N_2!}$$

and hence the free energy F = -kT ln (Z/N!) is extensive.

$$\ln\left(\frac{Z_c(N_1, V_1, N_2, V_2)}{(N_1 + N_2)!}\right) = \ln\left(\frac{Z_1}{N_1!}\right) + \ln\left(\frac{Z_2}{N_2!}\right)$$

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…and, of course, really indistinguishable particles (e.g ^{4}He atoms) can never be distinguished, not even in principle.

Hence, exchanging them also does not lead to a different macroscopic state.

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The path-integral approach

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How?

We have assumed qu[illegible] (discrete states) but often we are intereste[illegible] classical limit

$$\sum_i e^{-\beta E_i} \longrightarrow \frac{1}{h^{3N} N!} \int \int d\mathbf{p}^N \; d\mathbf{r}^N \; e^{-\beta \left[\sum_i \frac{p_i^2}{2m_i} + U(\mathbf{r}^N) \right]}$$

$\frac{1}{h^{3N}} \longrightarrow$ Volume of phase space

$\frac{1}{N!} \longrightarrow$ Particles are indistinguishable

Integration over the momenta can be carried out for most systems:

$$\int d\mathbf{p}^N \exp\left\{ -\beta \left[\sum_i \frac{p_i^2}{2m_i} \right] \right\} = \left[\int dp \exp\left\{ -\beta \frac{p^2}{2m} \right\} \right]^{3N} = \left(\frac{2\pi m}{\beta} \right)^{\frac{3}{2}N}$$

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Steps:

1. We can introduce functions of operators. E.g.

$$< i|e^{A}|i >= \sum_n < i|\frac{A^n}{n!}|i >$$

Example. For an energy eigenstate i:

$$< i|e^{-\beta H}|i >= \sum_n < i|\frac{(-\beta H)^n}{n!}|i >= \sum_n \frac{(-\beta E_i)^n}{n!} = e^{-\beta E_i}$$

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2. The "trace" of a quantum mechanical operator does not depend on the basis set

$$\sum_{\text{all } i} < i|A|i >= \sum_{\text{all } j} < j|A|j >$$

Example:

$$\sum_{\text{eigenstates i}} < i|e^{-\beta H}|i >= \sum_{\text{other states j}} < j|e^{-\beta H}|j >$$

$$Q = \sum_{\text{eigenstates i}} e^{-\beta E_i} = \sum_{\text{other states j}} < j|e^{-\beta H}|j >$$

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3. We can write the unit operator ***I*** as

$$I = \sum_{\text{complete set of states j}} |j><j|$$

Example:

$$I = \sum_{\text{all wavevectors q}} |q><q|$$

The momentum p is related to the wavevector q, via

$$\mathbf{p} = \hbar\mathbf{q} = \hbar\{n_x, n_y, n_z\}\frac{2\pi}{L}$$

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Now apply to partition function:

$$Q = \sum_{\text{eigenstates i}} e^{-\beta E_i} = \sum_{\text{other states j}} <j|e^{-\beta H}|j>$$

Choose for *j* the position eigenstates *r*:

$$Q = \frac{1}{N!}\sum_r <r|e^{-\beta H}|r>$$

This we cannot compute.

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Now write: *H* = *K* + *U,* then

$$Q = \frac{1}{N!}\sum_r < r|e^{-\beta(K+U)}|r >$$

This, we can still not compute. What we *can* compute is:

$$\sum_q < q|e^{-\beta K}|q > \approx \frac{V^N}{h^{3N}}\int dp^N e^{-\beta K}$$

or (possibly):

$$Z = \frac{1}{N!}\sum_r < r|e^{-\beta(U)}|r > = \frac{1}{N!}\int dr^N e^{-\beta U(r^N)}$$

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We could use these simplifications if:

$$e^{-\beta(K+U)} \stackrel{?}{=} e^{-\beta K}e^{-\beta U}$$

But for non-commuting operators A and B,

$$e^{A+B} \neq e^A e^B$$

However: in the classical limit, we can write

$$e^{-\beta(K+U)} \approx e^{-\beta K}e^{-\beta U}$$

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In the classical limit we get:

$$Q = \frac{1}{N!}\sum_r < r|e^{-\beta(K+U)}|r > \approx$$

$$\frac{1}{N!}\sum < r|e^{-\beta U}|r >< r|q >< q|e^{-\beta K}|q' >< q'|r >$$

$$\frac{1}{N!}\int dr^N e^{-\beta U(r^N)}\frac{V^N}{h^{3N}}\int dp^N e^{-\beta K} \times \frac{1}{V^N}$$

Or…

$$Q_{\text{classical}} = \frac{1}{h^{3N}N!}\int dr^N dp^N e^{-\beta\left[U(r^N)+K(p^N)\right]}$$

(back)

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