# Molecular Simulation

## Background

# Why Simulation?

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

# Example: computing the melting point of ice

Why bother?

This works better.

## *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.**

## *Testing approximate theories by:*

**Computer “experiments”**

# 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.

# The limits of Experiments

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

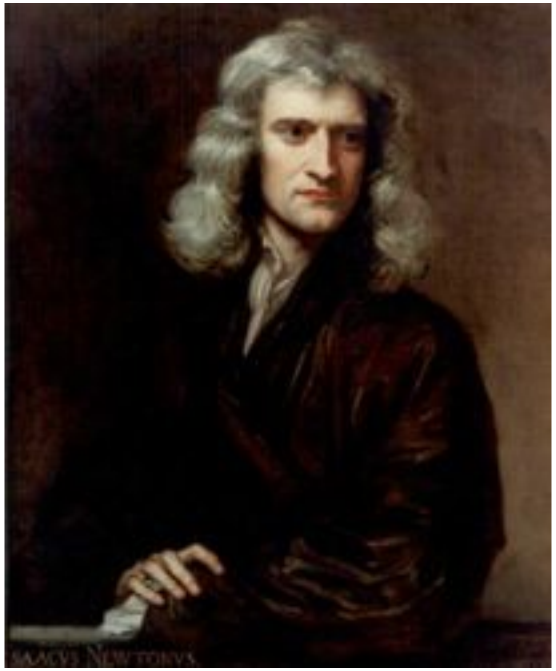
Result: “Experulation”.

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

# Why Simulation?

**We wish to predict the macroscopic properties of (classical) many-body systems.**

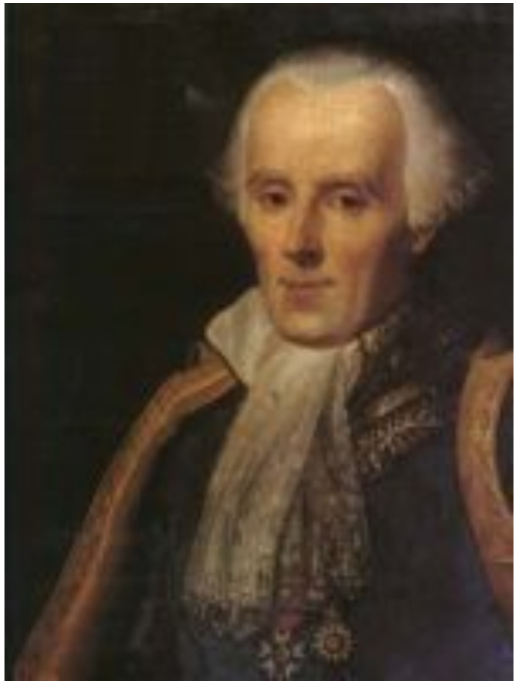
**Can this be done?**



# NEWTON: F=m a

## LAPLACE:

***Nous devons donc envisager l'état présent de l'universe comme l'effet de son état antérieur et comme la cause de delui qui va suivre. Une intelligence qui, pour un instant donné, connaîtrait toutes les forces dont la nature est animée et la situation respective des êtres qui las composent, si d'ailleurs elle était assez vaste pour soumettre ces données à l'Analyse, embrasserait dans la même formule les mouvements des plus grands corps de l'univers et ceux du plus lèger atome : rien ne serait incertain pour elle, et l'avenir, comme le passé, serait présent à ses yeux.***



*"Translation"* In principle "Yes".

Provided that we know the position, velocity and interaction of all molecules, then the future behavior is predictable,…**BUT**

# *…. There are so many molecules.*

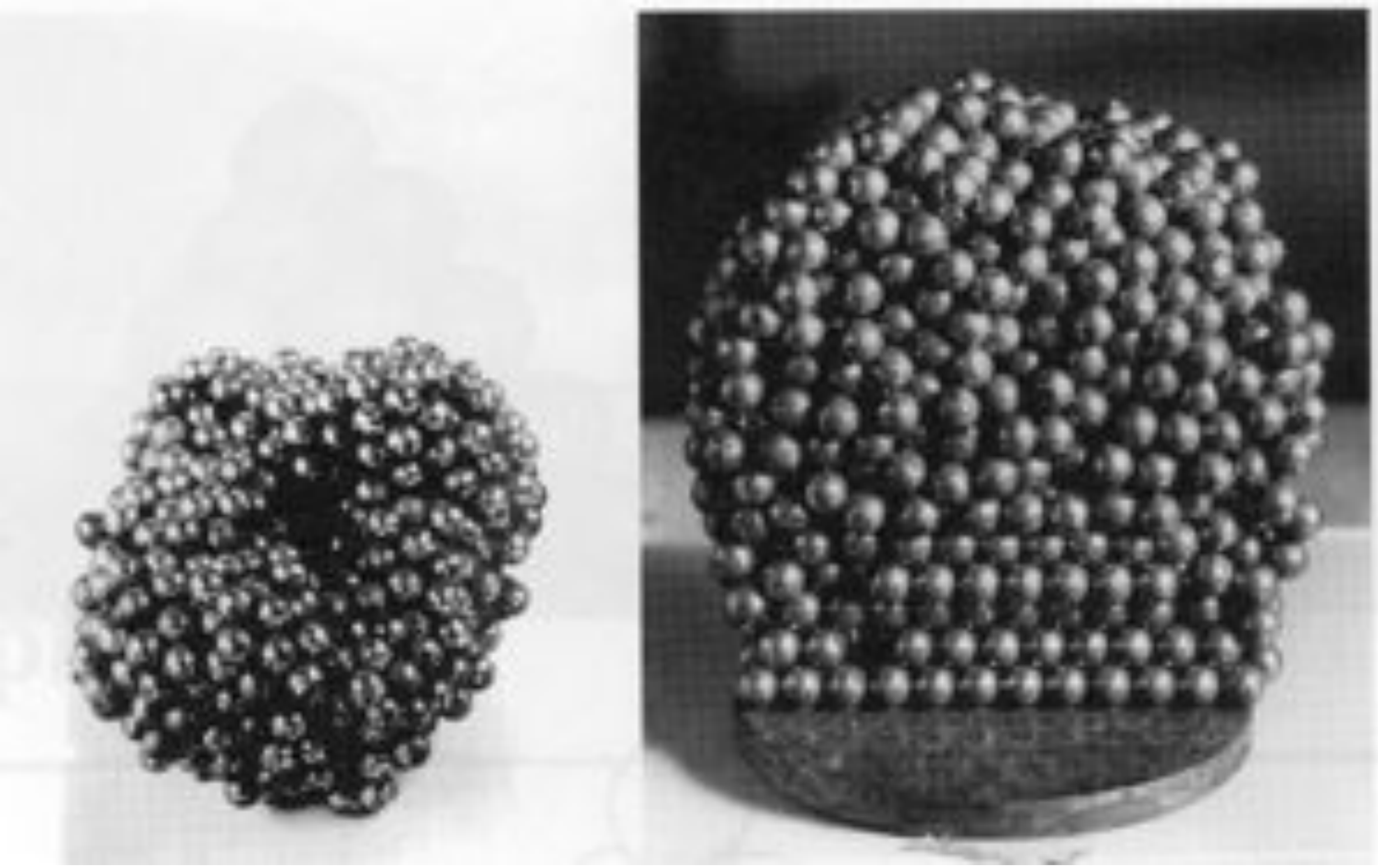
This is why, before the advent of the computer, it was impossible to predict the properties of real materials.

What was the alternative?

1. Smart tricks ("theory")

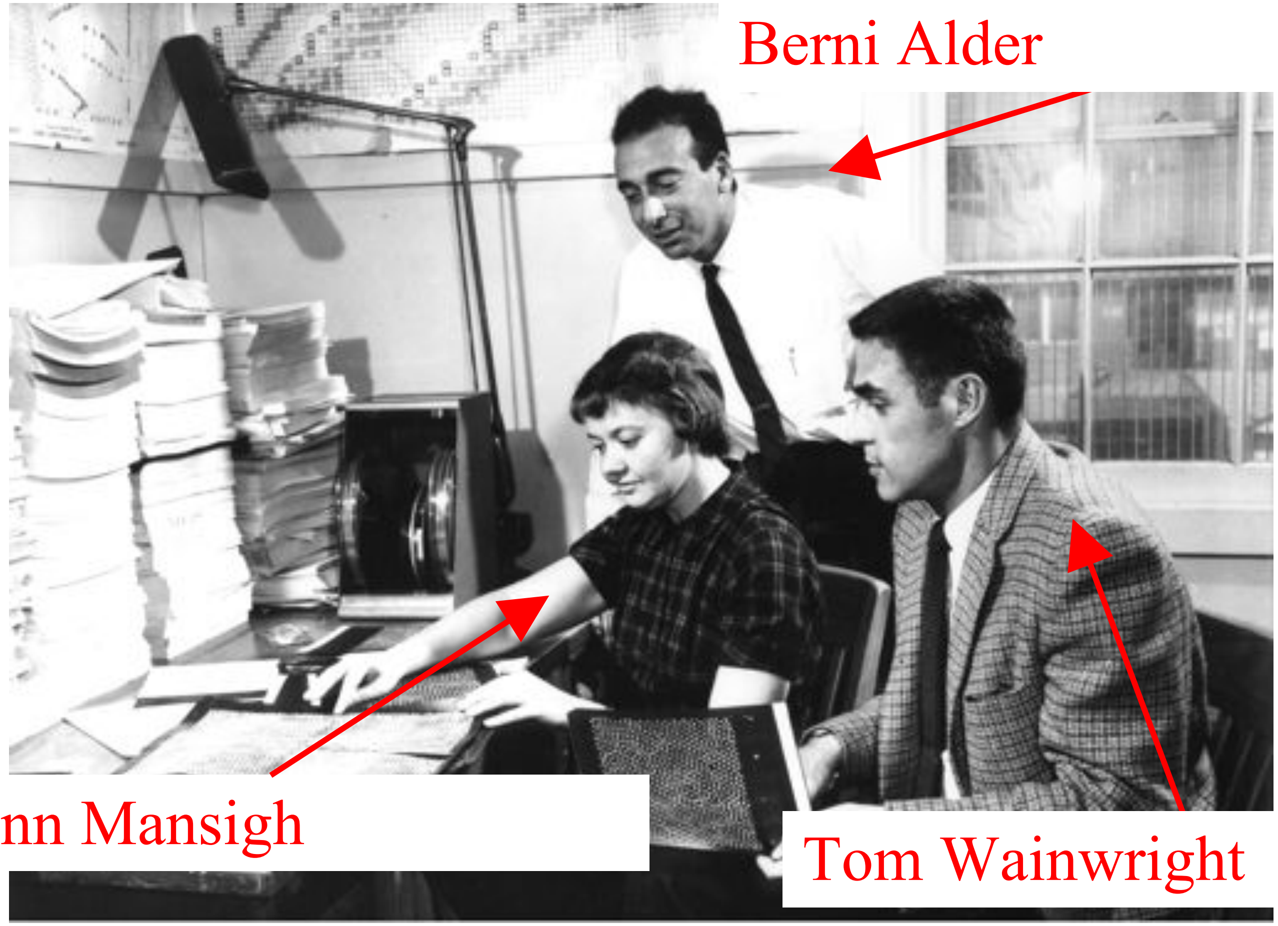
   Only works in special cases

2. Constructing model ("molecular lego")…



J.D. Bernal’s “ball-bearing model”
of an atomic liquid…

# The computer age (1953…)



Berni Alder

Mary-Ann Mansigh

Tom Wainwright

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

# Intermezzo:

# Essential Statistical Mechanics

**A brief summary of:**

**Entropy, temperature, Boltzmann distributions**
**and the Second Law of Thermodynamics**

The basics:

1. Nature is quantum-mechanical
2. Consequence:

   Systems have discrete quantum states.

   For finite "closed" systems, the number of states is finite (but usually very large)
3. Hypothesis: **In a closed system, every state is equally likely to be observed.**
4. Consequence: **ALL of equilibrium Statistical Mechanics and Thermodynamics**

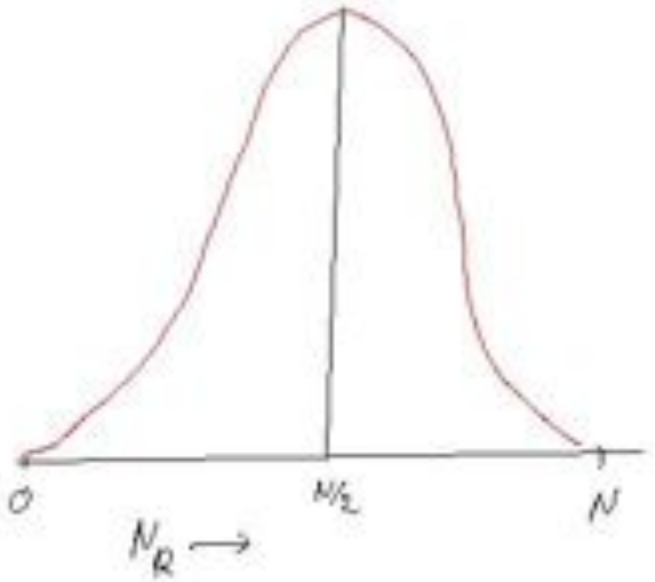
## First: **Simpler example (standard statistics)**

Draw N balls from an infinite vessel that contains an equal number of red and blue balls

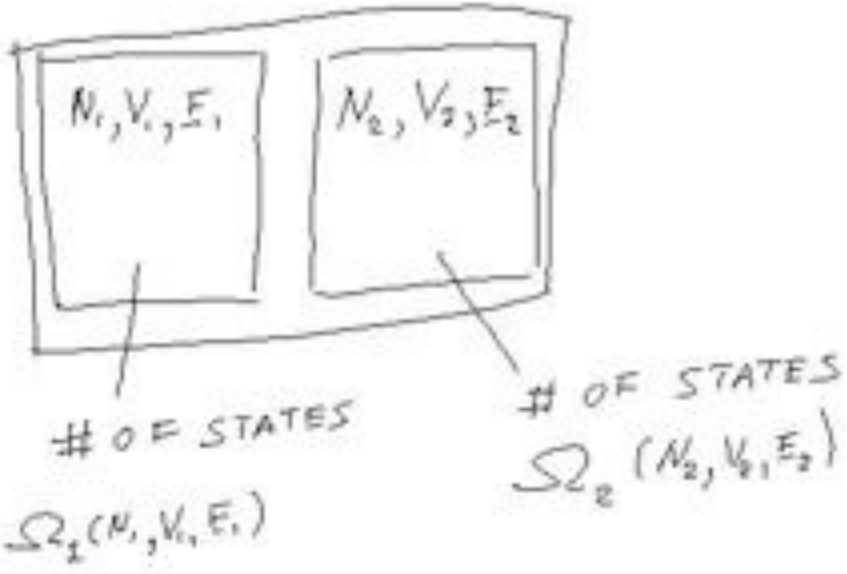
Number of possibilities to draw $N_R$ red balls and $N_B$ blue balls: $\Omega(N_R, N_B) = \frac{N!}{N_R! N_B!}$.

Most likely $N_R = N_B = N/2$.

$\Omega(N/2, N/2) = \frac{N!}{(N/2)!(N/2)!}$.

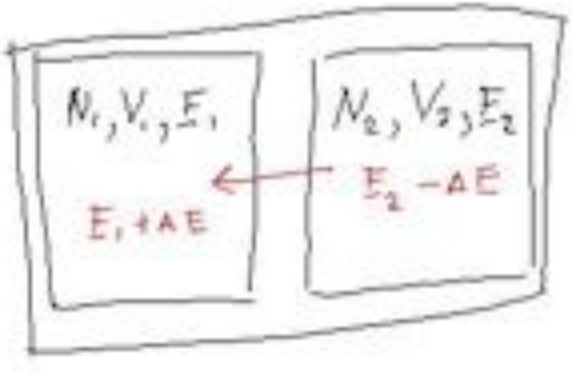


Now consider two systems with total energy **E**.



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

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



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 $\ln(\Omega_1 \times \Omega_2)$.

So:

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

With:

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

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

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")

Normally, thermal equilibrium means: equal temperatures…

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:

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…)

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

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

But we found (defined):

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

And 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.**

How large is Ω?

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

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

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

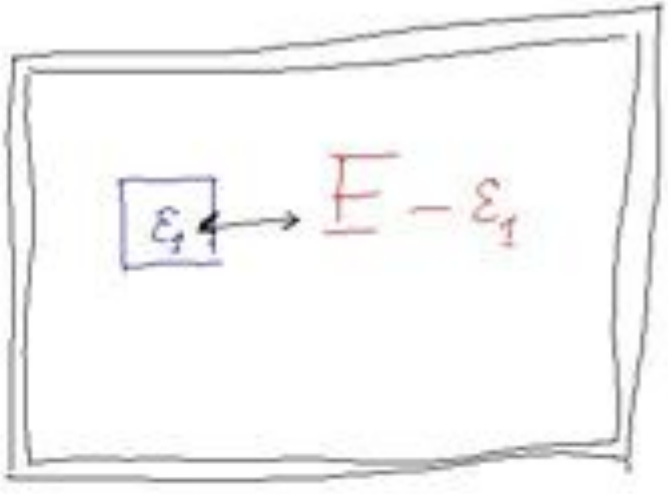
Macroscopic deviations from the second law of thermodynamics are not forbidden, but they are extremely unlikely.

A mathematical relation:

$$10^{-10^{23}} \neq 0$$

A physical relation:

$$10^{-10^{23}} = 0$$



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?

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

**But, as $\beta = 1/k_B T$ :**

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

The probability that the small system is in a **given** (“labeled”) state with energy $\varepsilon_i$ is

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

using

$$\Omega_B(E - \epsilon_i) = \Omega_B(E)\,\mathrm{exp}(-\epsilon_i/k_B T)$$

we get

$$P(\epsilon_i) = \frac{\mathrm{exp}(-\epsilon_i/k_B T)}{\sum_i \mathrm{exp}(-\epsilon_i/k_B T)}$$

This is the Boltzmann distribution:

“Low energies are more likely than high energies”

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

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

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

Hence, the average energy is

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

Therefore

$$< E >= -\frac{\partial \ln Q}{\partial \beta}$$

This can be compared to the thermodynamic relation

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

This suggests that the partition sum

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

is related to the Helmholtz free energy through

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

How?

We have assumed qua… …es (discrete states) but often we are interested i… …classical limit

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

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

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

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

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

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:

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

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

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

Example:

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

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

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

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

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.

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):

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

We could use these simplifications if:

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

But for non-commuting operators A and B,

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

However: in the classical limit, we can write

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

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…

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

# Remarks

Define *de Broglie* thermal wavelength:

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

Partition function:

$$Q\left(N,V,T\right) = \frac{1}{\Lambda^{3N} N!} \int \mathrm{d}\mathbf{r}^N \exp\left[ -\beta U\left(r^N\right) \right]$$

# Check: ideal gas

$$Q\left(N,V,T\right)=\frac{1}{\Lambda^{3N}N!}\int \mathrm{d}\mathbf{r}^{N}\exp\left[-\beta U\left(r^{N}\right)\right]$$

$$=\frac{1}{\Lambda^{3N}N!}\int \mathrm{d}\mathbf{r}^{N}1=\frac{V^{N}}{\Lambda^{3N}N!}$$

Free energy:

$$\beta F=-\ln\left(\frac{V^{N}}{\Lambda^{3N}N!}\right)\approx N\left(\ln\rho\Lambda^{3}-1\right)$$

Pressure:

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

Energy:

$$E=\left(\frac{\partial\beta F}{\partial\beta}\right)=\frac{3N}{\Lambda}\frac{\partial\Lambda}{\partial\beta}=\frac{3}{2}Nk_{B}T$$

# Relating macroscopic observables to microscopic quantities

Examples:

**Heat capacity**

**Pressure**

**Diffusion coefficient**

Fluctuation expression for heat capacity.

Recall:

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

with

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

Or should it be:

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

with

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

There is a problem with the notation.

Also with the internal energy: E or U.

Heat capacity:

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

Using our expression for **E:**

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

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 thus:

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

But you can also compute $C_V$ directly from

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

# COMPUTING THE PRESSURE:

$$F = -kT \ln Q$$

$$Q = \frac{1}{h^{3N} N!} \int \mathrm{d}\mathbf{r}^N \exp[-\mathcal{U}(\mathbf{r}^N)/k_B T]$$

$$\frac{\partial F}{\partial V} = -P$$

Introduce “scaled” coordinates:

$$\mathbf{r} \equiv L\mathbf{s}$$

$$Q(N,V,T) = \frac{V^N}{\Lambda^{3N} N!} \int d\mathrm{s}^N \ \exp[-\beta \mathcal{U}(\mathrm{s}^N; L)]$$

$$\frac{\partial F}{\partial V} = -P$$

$$\frac{\partial F}{\partial V} = k_B T \frac{\partial \ln Q}{\partial V}$$

$$Q(N,V,T) = \frac{V^N}{\Lambda^{3N} N!} \int d\mathrm{s}^N \; \exp[-\beta \mathcal{U}(\mathrm{s}^N; L)]$$

$$P = k_B T \frac{\partial \ln V^N \int d\mathbf{s}^N \; \exp[-\beta \mathcal{U}(\mathbf{s}^N; L)]}{\partial V}$$

$$P = \frac{N k_B T}{V} + k_B T \frac{\partial \ln \int d\mathbf{s}^N \; \exp[-\beta \mathcal{U}(\mathbf{s}^N; L)]}{\partial V}$$

$$\frac{\partial \mathcal{U}(\mathbf{s}^N; L)}{\partial V} = \sum_{i=1}^{N} \frac{\partial \mathcal{U}(\mathbf{r}^N)}{\partial \mathbf{r}_i} \frac{\partial \mathbf{r}_i}{\partial V}$$

$$\frac{\partial \mathbf{r}_i}{\partial V} = \frac{1}{3L^2} \frac{\partial L \mathbf{s}_i}{\partial L} = \frac{1}{3L^2} \mathbf{s}_i$$

$$\frac{\partial \mathcal{U}(\mathbf{s}^N; L)}{\partial V} = \sum_{i=1}^{N} \frac{\partial \mathcal{U}(\mathbf{r}^N)}{\partial \mathbf{r}_i} \cdot \frac{\mathbf{r}_i}{3V}$$

$$P = \frac{N k_B T}{V} + k_B T \frac{\partial \ln \int d\mathbf{s}^N \ \exp[-\beta \mathcal{U}(\mathbf{s}^N; L)]}{\partial V}$$

$$P = \frac{N k_B T}{V}$$

$$- \frac{\int d\mathbf{s}^N \ \sum_{i=1}^N \frac{\partial \mathcal{U}(\mathbf{r}^N)}{\partial \mathbf{r}_i} \cdot \frac{\mathbf{r}_i}{3V} \exp[-\beta \mathcal{U}(\mathbf{s}^N; L)]}{\int d\mathbf{s}^N \ \exp[-\beta \mathcal{U}(\mathbf{s}^N; L)]}$$

$$P = \frac{N k_B T}{V} - \left\langle \sum_{i=1}^N \frac{\partial \mathcal{U}(\mathbf{r}^N)}{\partial \mathbf{r}_i} \cdot \frac{\mathbf{r}_i}{3V} \right\rangle$$

$$P = \frac{N k_B T}{V} + \frac{1}{3V} \left\langle \sum_{i=1}^N \mathbf{f}_i \cdot \mathbf{r}_i \right\rangle$$

$$P = \frac{Nk_BT}{V} + \frac{1}{3V}\left\langle \sum_{i=1}^{N} \mathbf{f}_i \cdot \mathbf{r}_i \right\rangle$$

For pairwise additive forces:

$$\mathbf{f}_i = \sum_{j \neq i} \mathbf{f}_{ij}$$

Then

$$P = \frac{Nk_BT}{V} + \frac{1}{3V}\left\langle \sum_{i,j=1,i\neq j}^{N} \mathbf{f}_{ij} \cdot \mathbf{r}_i \right\rangle$$

$$P = \frac{N k_B T}{V} + \frac{1}{3V} \left\langle \sum_{i,j=1, i\neq j}^{N} \mathbf{f}_{ij} \cdot \mathbf{r}_i \right\rangle$$

*i* and *j* are dummy variable hence:

$$\sum_{i,j=1, i\neq j}^{N} \mathbf{f}_{ij} \cdot \mathbf{r}_i = \sum_{j,i=1, j\neq i}^{N} \mathbf{f}_{ji} \cdot \mathbf{r}_j$$

And we can write

$$\sum_{i,j=1, i\neq j}^{N} \mathbf{f}_{ij} \cdot \mathbf{r}_i = \frac{1}{2} \sum_{j,i=1, j\neq i}^{N} \left( \mathbf{f}_{ij} \cdot \mathbf{r}_i + \mathbf{f}_{ji} \cdot \mathbf{r}_j \right)$$

But as action equals reaction (Newton's 3rd law):

$$\mathbf{f}_{ij} = -\mathbf{f}_{ji}$$

And hence

$$\sum_{j,i=1,j\neq i}^{N} \left(\mathbf{f}_{ij} \cdot \mathbf{r}_i + \mathbf{f}_{ji} \cdot \mathbf{r}_j\right) = \sum_{j,i=1,j\neq i}^{N} \mathbf{f}_{ij} \cdot (\mathbf{r}_i - \mathbf{r}_j)$$

Inserting this in our expression for the pressure, we get:

$$P = \frac{N k_B T}{V} + \frac{1}{6V} \left\langle \sum_{i,j=1,i\neq j}^{N} \mathbf{f}_{ij} \cdot \mathbf{r}_{ij} \right\rangle$$

Where $\mathbf{r}_{ij} \equiv \mathbf{r}_i - \mathbf{r}_j$

# What to do if you cannot use the virial expression?

$$P = -\frac{\partial F}{\partial V} \approx \frac{F(V - \Delta V) - F(V)}{\Delta V}$$

When is it not possible to use the virial expression?

# Other ensembles?

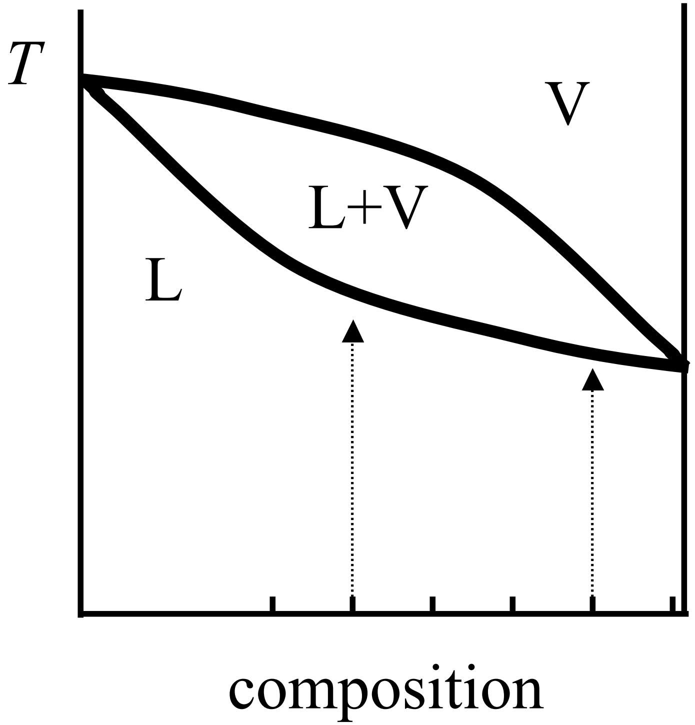
In the thermodynamic limit the thermodynamic properties are independent of the ensemble.

However, it is useful to select an appropriate ensemble for a given experimental condition.

It is important to know how to simulate in the various ensembles.

But for doing this we need to know the Statistical Thermodynamics of the various ensembles.

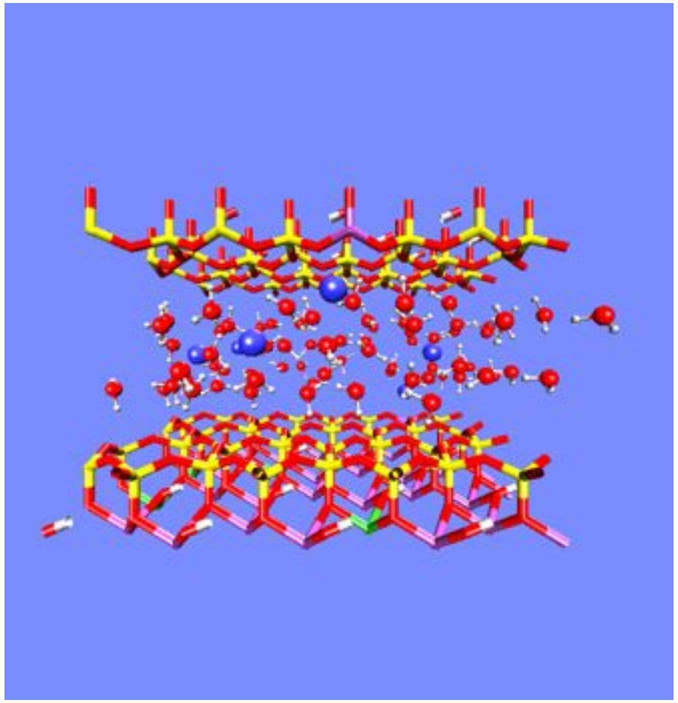
# Example (1): vapour-liquid equilibrium mixture



Measure the composition of the coexisting vapour and liquid phases if we start with a homogeneous liquid of two different compositions:

- How to mimic this with the *N,V,T* ensemble?
- What is a better ensemble?

# Example (2):
# adsorption of water in porous medium



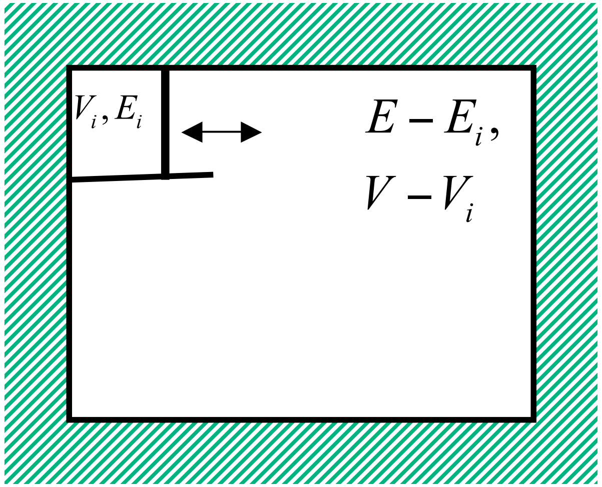
Clay layers can swell upon adsorption of water:

- How to mimic this in the $N, V, T$ ensemble?
- What is a better ensemble to use?

# Ensembles

- Micro-canonical ensemble: $E,V,N$
- Canonical ensemble: $T,V,N$
- Constant pressure ensemble: $T,P,N$
- Grand-canonical ensemble: $T,V,\mu$

# Constant pressure simulations: $N,P,T$ ensemble



Consider a small system that can exchange volume and energy with a large reservoir

$$\ln\Omega\left(V-V_{i,}E-E_i\right)=\ln\Omega\left(V,E\right)-\left(\frac{\partial\ln\Omega}{\partial E}\right)_V E_i-\left(\frac{\partial\ln\Omega}{\partial V}\right)_E V_i+\cdots$$

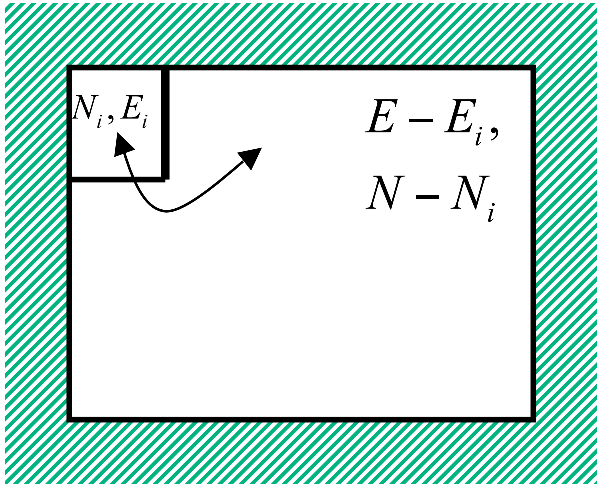
$$\ln\frac{\Omega\left(E-E_i,V-V_i\right)}{\Omega\left(E,V\right)}=-\frac{E_i}{k_BT}-\frac{pV_i}{k_BT}$$

Hence, the probability to find $E_i, V_i$:

$$P\left(E_i,V_i\right)=\frac{\Omega\left(E-E_i,V-V_i\right)}{\sum_{j,k}\Omega\left(E-E_j,V-V_k\right)}=\frac{\exp\left[-\beta\left(E_i+pV_i\right)\right]}{\sum_{j,k}\exp\left[-\beta\left(E_j+pV_k\right)\right]}$$

$$\propto\exp\left[-\beta\left(E_i+pV_i\right)\right]$$

# Grand-canonical simulations: $\mu, V, T$ ensemble



Consider a small system that can exchange *particles* and energy with a large reservoir

$$\ln \Omega\left(N - N_{i,} E - E_i\right) = \ln \Omega\left(N, E\right) - \left(\frac{\partial \ln \Omega}{\partial E}\right)_N E_i - \left(\frac{\partial \ln \Omega}{\partial N}\right)_E N_i + \cdots$$

$$\ln \frac{\Omega(E-E_i,N-N_i)}{\Omega(E,N)} = -\frac{E_i}{k_B T} + \frac{\mu N_i}{k_B T}$$

Hence, the probability to find $E_i$,$N_i$:

$$\begin{aligned} P(E_i, N) &= \frac{\Omega(E - E_i, N - N_i)}{\sum_{j,k} \Omega(E - E_i, N - N_k)} = \frac{\exp\left[-\beta(E_i - \mu N_i)\right]}{\sum j, k \exp\left[-\beta(E_j - \mu N_k)\right]} \\ &\sim \exp\left[-\beta(E_i - \mu N_i)\right] \end{aligned}$$

# Computing transport coefficients from an EQUILIBRIUM simulation.

How?

Use linear response theory (i.e. study decay of fluctuations in an equilibrium system)

## Linear response theory in 3 slides:

**Consider the response of an observable A due to an external field $f_B$ that couples to an observable B:**

$$H = H_0 - f_B B$$

For simplicity, assume that $\langle A \rangle_0 = \langle B \rangle_0 = 0$

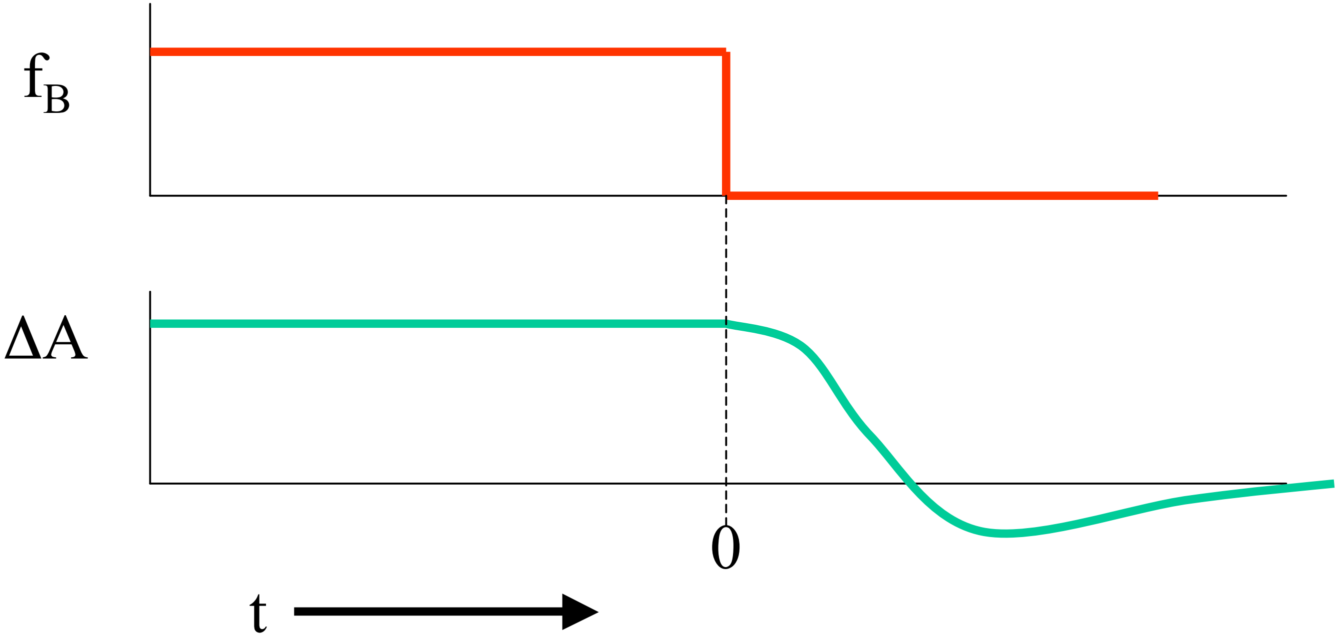
$$\langle \Delta A \rangle_{f_B} = \frac{\int \exp[-\beta(H_0 - f_B B)] A}{\int \exp[-\beta(H_0 - f_B B)]}$$

For small $f_B$ we can linearize:

$$\langle \Delta A \rangle \approx \beta f_B \frac{\int \exp[-\beta H_0] B A}{\int \exp[-\beta H_0]}$$

Hence $\langle \Delta A \rangle \approx \beta f_B \langle BA \rangle_0$

Now consider a weak field that is switched off at t=0.



Using exactly the same reasoning as in the static case, we find:

$$\langle \Delta A \rangle (t) = \beta f_B \langle B A(t) \rangle_0$$

# Simple example: Diffusion

Average total displacement:

$$< \Delta x >= \sum_{i=1}^{N} < \Delta x_i >= 0$$

Mean squared displacement:

$$< \Delta x^2 >=< \left( \sum_{i=1}^{N} \Delta x_i \right)^2 >$$

$$= \sum_{i=1}^{N} < \Delta x_i^2 >= Na^2$$

## Macroscopic diffusion equations

**Fick’s laws:**

$$\frac{\partial c(x,t)}{\partial t} + \frac{\partial\ j_x(x,t)}{\partial x} = 0.$$

(conservation law)

$$j_x(x,t) = -D\frac{\partial\ c(x,t)}{\partial x}$$

(constitutive law)

Combine:

$$\frac{\partial\, c(x,t)}{\partial\, t} - D\frac{\partial^2\, c(x,t)}{\partial\, x^2} = 0.$$

Initial condition:

$$c(x,0) = \delta(x)$$

Solve:

$$c(x,t) = \frac{1}{(4\pi D t)^{1/2}} \exp\left(-\frac{x^2}{4Dt}\right)$$

Compute mean-squared width:

$$\left\langle x^2(t) \right\rangle \equiv \int dx\; c(x,t) x^2$$

$$\frac{\partial}{\partial t}\int dx\; x^2 c(x,t) = D\int dx\; x^2 \frac{\partial^2 c(x,t)}{\partial\, x^2}.$$

$$\Updownarrow$$

$$\frac{d\left\langle x^2(t)\right\rangle}{dt}.$$

Integrating the left-hand side by parts:

Or:

$$2D = \lim_{t \to \infty} \frac{d \left\langle x^2(t) \right\rangle}{dt}$$

This is how Einstein proposed to measure the diffusion coefficient of Brownian particles

$$\Delta x(t) = \int_0^t dt'\, v_x(t').$$

$$2D = \lim_{t\to\infty} \frac{\partial \left\langle x^2(t) \right\rangle}{\partial t}$$

$$\left\langle x^2(t) \right\rangle = \left\langle \left( \int_0^t dt'\, v_x(t') \right)^2 \right\rangle$$

$$\left\langle \left( \int_0^t dt'\, v_x(t') \right)^2 \right\rangle =$$

$$= \int_0^t \int_0^t dt' dt'' \left\langle v_x(t') v_x(t'') \right\rangle$$

$$= 2 \int_0^t \int_0^{t'} dt' dt'' \left\langle v_x(t') v_x(t'') \right\rangle .$$

$$\left\langle v_x(t') v_x(t'') \right\rangle = \left\langle v_x(t' - t'') v_x(0) \right\rangle .$$

$$2D = \lim_{t\to\infty} 2 \int_0^t dt'' \left\langle v_x(t - t'') v_x(0) \right\rangle$$

$$D = \int_0^\infty d\tau \ \langle v_x(\tau) v_x(0) \rangle$$

(“Green-Kubo relation”)

Other examples: shear viscosity

$$\eta = \frac{1}{Vk_BT}\int_0^\infty dt \ \langle \sigma^{xy}(0)\sigma^{xy}(t)\rangle$$

$$\sigma^{xy} = \sum_{i=1}^{N}\left(m_i v_i^x v_i^y + \frac{1}{2}\sum_{j\neq i} x_{ij} f_y(r_{ij})\right)$$

## Other examples: thermal conductivity

$$\lambda_T = \frac{1}{V k_B T^2} \int_0^\infty dt \ \langle j_z^e(0) j_z^e(t) \rangle$$

$$j_z^e = \frac{d}{dt} \sum_{i=1}^{N} z_i \frac{1}{2} \left( m_i v_i^2 + \sum_{j \neq i} v(r_{ij}) \right)$$

Other examples: electrical conductivity

$$\sigma_e = \frac{1}{V k_B T} \int_0^\infty dt \ \left\langle j_x^{\mathrm{el}}(0) j_x^{\mathrm{el}}(t) \right\rangle$$

$$j_x^{\mathrm{el}} = \sum_{i=1}^{N} q_i v_i^x .$$