

Understanding Molecular Simulation:
Lecture 8: Advanced Methods

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**I will focus on:
Computer “measurements”**

1. What and what not ?
2. How ?

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Simulations are used to predict observable properties, or to test theoretical predictions

To this end, we must *measure* observables in simulations.

Measurements in a computer simulation resemble experimental measurements:

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- We have to prepare a sample,
- We have to decide on the best measuring technique,
- We have to accumulate enough data,
- and we should analyse the effect of possible systematic and statistical errors in our results.



For these reasons, we use the word *measurement* to refer to the calculation of an observable, mainly for lack of a better word

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It is easy to spend an entire course on simulation measurements.

So this lecture will only present a few (hopefully important) examples.

Even so, I will run out of time, but please feel free to ask/comment.

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Experimental measurements: we look at the response of a macroscopic instrument.

Simulation measurements are usually VERY different:

We relate the observable to the coordinates and momenta of the particles that we can read out from our simulation.

HOW ?

That is the subject of this lecture.

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First the easy ones

Density: number of particles per unit volume

$$\rho = (N/V)$$

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Temperature - how is it defined?

Start with thermodynamics

$$dS = \frac{1}{T}dE + \frac{P}{T}dV - \frac{\mu}{T}dN$$

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

Statistical mechanics: $S = k_B \ln \Omega(E, V, N)$

We now focus on the entropy associated with the kinetic energy:

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$$\Omega(E, V, N) = \text{constant} \times \int d\mathbf{p}^N \delta(E - \sum_i p_i^2/2m)$$

Ω is a hypersphere in momentum space, with radius $(2mE)^{1/2}$

The volume contained in this hypersphere is $\sim (2mE)^{dN/2}$

and hence its surface area $\Omega \sim (2mE)^{[dN-1]/2}$

It then follows that

$$1/T = k_B \left(\frac{\partial \ln \Omega(E, V, N)}{\partial E} \right) = k_B \frac{(dN-1)/2}{E}$$

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Finally, we get:

$$k_B T/2 = \frac{E}{dN-1} \equiv E/f$$

Where f denotes the number of degrees of freedom ($f = N d - 1$), and E is the kinetic energy.

In most simulations with periodic boundary conditions, both energy **and** momentum are conserved. Then

$$f = (N-1) d - 1$$

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But how do we compute the kinetic energy?

That seems a strange question. Surely, we can compute

$$E = \sum_{i=1}^n \frac{1}{2} m v_i^2$$

That expression is correct as the timestep $\Delta t \Rightarrow 0$.

But for a finite timestep,

$$\frac{1}{2} m \langle v_i^2 \rangle \neq d k_B T / 2 \quad (d = \text{dimensionality})$$

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The reason is very interesting, and I would love to explain it, but it would take more time than we can spare

So, I just show an example that shows that the velocity estimate of the kinetic energy yields incorrect temperature estimates

2046 *J. Chem. Theory Comput.*, Vol. 6, No. 7, 2010

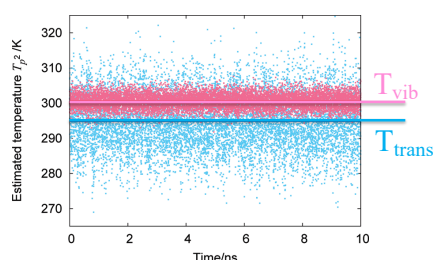


Figure 1. A hot solvent–cold protein problem. Temperatures of the protein ubiquitin (blue points) and water solvent (red points) are shown as a function of simulation time. Data were taken from an all-atom constant energy simulation that used velocity-Verlet integration with a 2 fs time step and bonds to hydrogen constrained; more details are given in Section 3.2.

Eastman et al., J. Chem. Theory Comput. **2010**, *6*, 2045

Gans/Shalloway, *PRE* **2000**, *61*, 614587.

The “apparent” vibrational temperature inside a protein (ubiquitin) is 6K higher than that of the solvent !

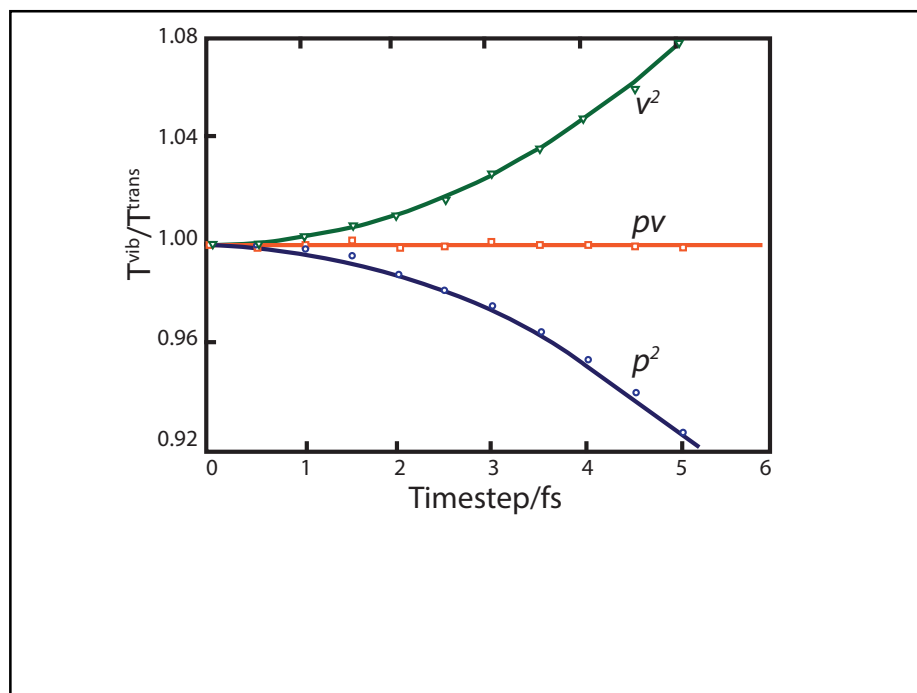
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The reason is (roughly) that, for a discrete (Velocity-Verlet) algorithm, $v_i \neq p_i/m$

A much better temperature estimate is obtained if we use the relation $k_B T = \langle p_i v_i \rangle$

But then v_i must be computed by differentiating a smooth interpolation of the discretized trajectory.

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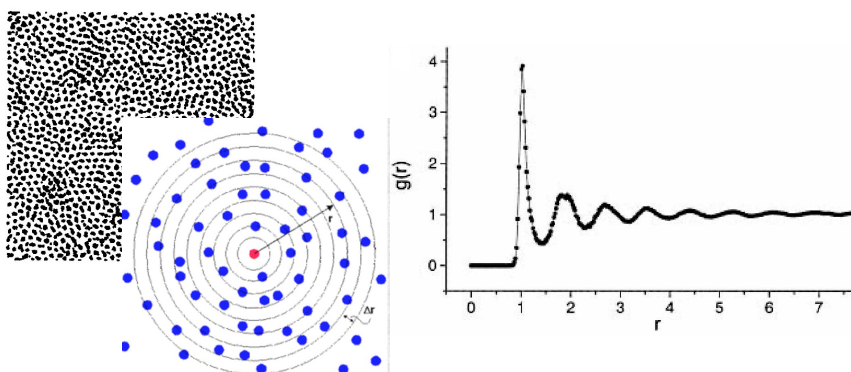
Questions/comments/... ?

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Sampling observable quantities:

Example 2: **the radial distribution function $g(r)$**

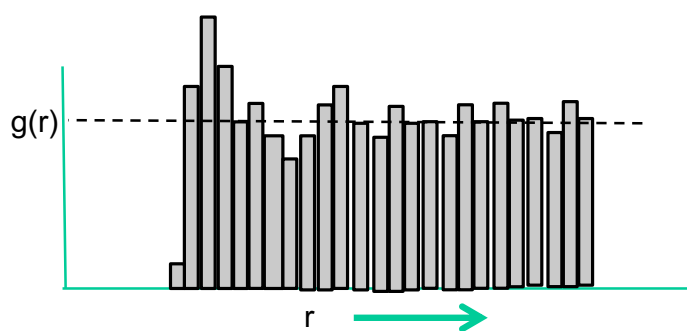
$g(r)$ = the average density at distance r from a particle, divided by the bulk density. In an ideal gas, $g(r) = 1$



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What could be simpler than computing a radial distribution function?

Just make a histogram of the densities as a function of distance



The noise is determined by Poisson statistics.

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Can we do better?

Yes

D. Borgis et al. Mol Phys 111, 3486 (2013)

D. de las Heras & M. Schmidt, Phys Rev

Lett 120, 218001 (2018)

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We start from:

$$g(r) = \frac{1}{\rho} \int d\hat{\mathbf{r}} \langle \rho(\mathbf{r}) \rangle_{N-1} = \frac{1}{\rho} \int d\hat{\mathbf{r}} \left\langle \sum_{j \neq i} \delta(\mathbf{r} - \mathbf{r}_j) \right\rangle_{N-1}$$

where I have picked a random particle i as the origin

The derivative of $g(r)$ with respect to r is:

$$\left(\frac{\partial g(r)}{\partial r} \right) = \frac{1}{\rho} \frac{\partial}{\partial r} \int d\hat{\mathbf{r}} \left\langle \sum_{j \neq i} \delta(\mathbf{r} - \mathbf{r}_j) \right\rangle$$

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The only term in the integral that depends on r is the delta-function

$$\left(\frac{\partial g(r)}{\partial r} \right) = \frac{1}{\rho} \int d\hat{\mathbf{r}} \left\langle \sum_{j \neq i} \hat{\mathbf{r}} \cdot \nabla_{\mathbf{r}} \delta(\mathbf{r} - \mathbf{r}_j) \right\rangle$$

Now we can write:

$$\begin{aligned} \left(\frac{\partial g(r)}{\partial r} \right) &= \frac{1}{\rho} \frac{\int d\hat{\mathbf{r}} \int d\mathbf{r}^{N-1} e^{-\beta U(\mathbf{r}^N)} \sum_{j \neq i} \hat{\mathbf{r}} \cdot \nabla_{\mathbf{r}} \delta(\mathbf{r} - \mathbf{r}_j)}{\int d\mathbf{r}^{N-1} e^{-\beta U(\mathbf{r}^N)}} \\ &= \frac{\downarrow}{\rho} \frac{\int d\hat{\mathbf{r}} \int d\mathbf{r}^{N-1} e^{-\beta U(\mathbf{r}^N)} \sum_{j \neq i} \hat{\mathbf{r}} \cdot \nabla_{\mathbf{r}_j} \delta(\mathbf{r} - \mathbf{r}_j)}{\int d\mathbf{r}^{N-1} e^{-\beta U(\mathbf{r}^N)}} \end{aligned}$$

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Next, we perform partial integration with respect to \mathbf{r}_j :

$$= \frac{-\beta \int d\hat{\mathbf{r}} \int d\mathbf{r}^{N-1} e^{-\beta U(\mathbf{r}^N)} \sum_{j \neq i} \delta(\mathbf{r} - \mathbf{r}_j) \hat{\mathbf{r}} \cdot \nabla_{\mathbf{r}_j} U(\mathbf{r}^N)}{\int d\mathbf{r}^{N-1} e^{-\beta U(\mathbf{r}^N)}}$$

and the result is

$$\left(\frac{\partial g(r)}{\partial r} \right) = \frac{\beta}{\rho} \int d\hat{\mathbf{r}} \left\langle \sum_{j \neq i} \delta(\mathbf{r} - \mathbf{r}_j) \hat{\mathbf{r}}_j \cdot \mathbf{F}_j(\mathbf{r}^N) \right\rangle_{N-1}$$

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We can now obtain $g(r)$ by integration:

$$g(r) = g(r=0) + \frac{\beta}{\rho} \int_0^r dr' \int d\hat{\mathbf{r}}' \left\langle \sum_{j \neq i} \delta(\mathbf{r}' - \mathbf{r}_j) F_j^{(r')}(\mathbf{r}^N) \right\rangle_{N-1}$$

$$= g(r=0) + \frac{\beta}{\rho} \sum_j \left\langle \theta(r - r_j) \frac{F_j^{(r)}(\mathbf{r}^N)}{4\pi r_j^2} \right\rangle_{N-1}$$

$$= g(r=0) + \frac{\beta}{\rho} \int_{r' < r} d\mathbf{r}' \left\langle \frac{\sum_{j \neq i} \delta(\mathbf{r}' - \mathbf{r}_j) F_j^{(r')}(\mathbf{r}^N)}{4\pi r'^2} \right\rangle_{N-1}$$

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But the particle index i was just a dummy index, so we can write:

$$g(r) = g(r=0) + \frac{\beta}{N\rho} \sum_{i=1}^N \sum_{j \neq i} \left\langle \theta(r - r_{ij}) \frac{F_j^{(r)}(\mathbf{r}^N)}{4\pi r_{ij}^2} \right\rangle_{N-1}$$

Or, symmetrizing and i and j :

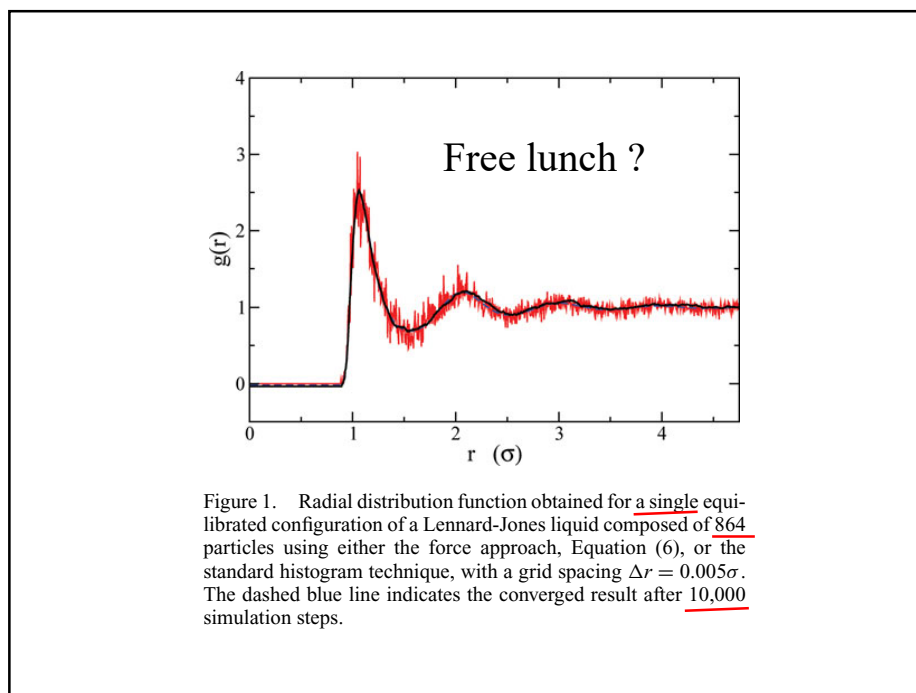
$$g(r) = g(r=0) + \frac{\beta}{2N\rho} \sum_{i=1}^N \sum_{j \neq i} \left\langle \theta(r - r_{ij}) \frac{F_j^{(r)}(\mathbf{r}^N) - F_i^{(r)}(\mathbf{r}^N)}{4\pi r_{ij}^2} \right\rangle_{N-1}$$

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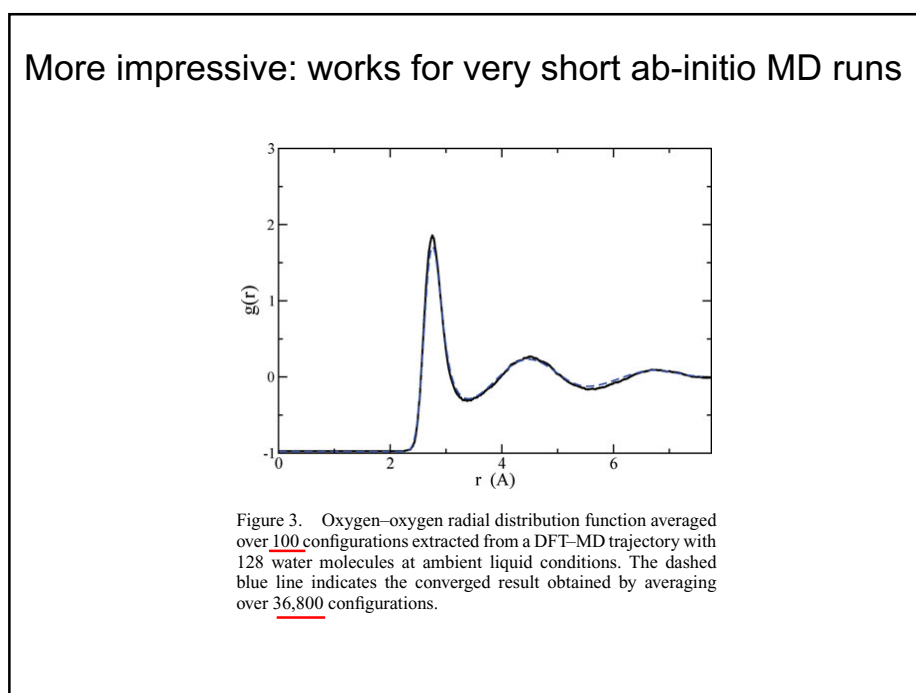
Note that $g(r)$ depends not just on the number of pairs *at* distance r , but on *all* pair distances less than r

I have *not* assumed that the interactions in the system are pairwise additive: $F_i - F_j$ is *not* a pair force.

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Scattering experiments and the structure factor:

The intensity of the scattered radiation (X-rays, neutrons, light ...) with wave-vector $q=2\pi/\lambda$ is proportional to $I(\mathbf{q}) = \langle |\mathbf{A}(\mathbf{q})|^2 \rangle$ with:

$$A(\mathbf{q}) \sim \sum_{i=1}^N b_i(q) e^{i\mathbf{q} \cdot \mathbf{r}_i}$$

If $b(q)$ is constant, we can factor it out and we get

$$\begin{aligned} A(\mathbf{q}) &\sim \sum_{i=1}^N e^{i\mathbf{q} \cdot \mathbf{r}_i} = \int d\mathbf{r} \sum_{i=1}^N \delta(\mathbf{r} - \mathbf{r}_i) e^{i\mathbf{q} \cdot \mathbf{r}} \\ &\equiv \int d\mathbf{r} \rho(\mathbf{r}) e^{i\mathbf{q} \cdot \mathbf{r}} \end{aligned}$$

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$$I(q) \sim S(\mathbf{q}) = \frac{1}{N} [\langle |\rho(\mathbf{q})|^2 \rangle - |\langle \rho(\mathbf{q}) \rangle|^2]$$

$$= \frac{1}{N} \int_V \int_V d\mathbf{r} d\mathbf{r}' [\langle \rho(\mathbf{r}) \rho(\mathbf{r}') \rangle - \langle \rho \rangle^2] e^{i\mathbf{q} \cdot (\mathbf{r} - \mathbf{r}')}$$

In isotropic liquids: $\langle \rho(\mathbf{r}) \rho(\mathbf{r}') \rangle \equiv \rho^2 g(|\mathbf{r} - \mathbf{r}'|)$

And hence:

$$S(q) = \rho \int_V d\mathbf{r} [g(r) - 1] e^{i\mathbf{q} \cdot \mathbf{r}}$$

That looks great: we can determine the structure factor $S(q)$ from $g(r)$

DON'T

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Always use:

$$S(\mathbf{q}) = \frac{1}{N} [\langle |\rho(\mathbf{q})|^2 \rangle - |\langle \rho(\mathbf{q}) \rangle|^2]$$

Why ?

Because truncating $g(r)$ in the Fourier transform may lead to spurious oscillations (even negative values) of $S(q)$ – and $S(q)$ is a variance, and hence non-negative.

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Sampling observable
quantities:

Pressure

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1. Thermodynamic relation:

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

2. Statistical mechanical relation:

$$F = -k_B T \ln Q(N, V, T)$$

With (for atomic systems):

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

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Introduce “scaled” coordinates:

$$\mathbf{s}_i = \mathbf{r}_i / L$$

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

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Then:

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

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

How does the second term depend on V ?

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$$\frac{\partial \mathcal{U}(s^N)}{\partial V} = \sum_{i=1}^N \frac{\partial \mathcal{U}(\mathbf{r}^N)}{\partial \mathbf{r}_i} \frac{\partial \mathbf{r}_i}{\partial V} + \left(\frac{\partial \mathcal{U}}{\partial V} \right)_{s_i, N, T}$$

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

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

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

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$$P = \frac{Nk_B T}{V}$$

$$= \frac{\int ds^N \sum_{i=1}^N \frac{\partial \mathcal{U}(\mathbf{r}^N)}{\partial \mathbf{r}_i} \cdot \frac{\mathbf{r}_i}{3V} \exp[-\beta \mathcal{U}(\mathbf{s}^N)]}{\int ds^N \exp[-\beta \mathcal{U}(\mathbf{s}^N)]} - \left\langle \left(\frac{\partial \mathcal{U}}{\partial V} \right)_{\mathbf{s}_i} \right\rangle_{N,T}$$

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

$$P = \frac{Nk_B T}{V} + \frac{1}{3V} \left\langle \sum_{i=1}^N \mathbf{f}_i \cdot \mathbf{r}_i \right\rangle - \left\langle \left(\frac{\partial \mathcal{U}}{\partial V} \right)_{\mathbf{s}_i} \right\rangle_{N,T}$$

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$$P = \frac{Nk_B T}{V} + \frac{1}{3V} \left\langle \sum_{i=1}^N \mathbf{f}_i \cdot \mathbf{r}_i \right\rangle - \left\langle \left(\frac{\partial \mathcal{U}}{\partial V} \right)_{\mathbf{s}_i} \right\rangle_{N,T}$$

For pairwise additive forces:

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

Then

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

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

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

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

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

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

And hence

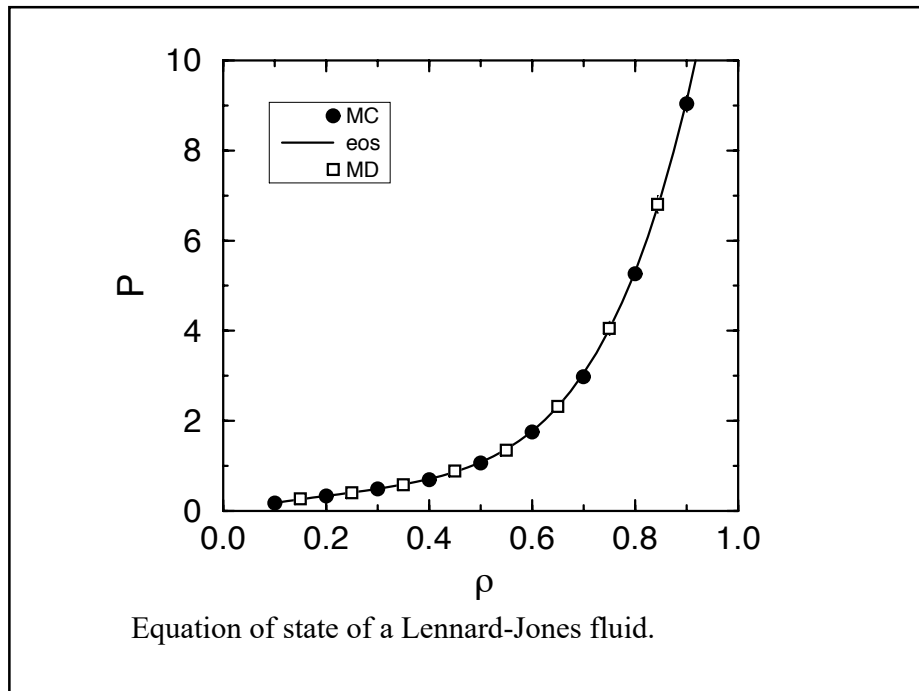
$$\sum_{j,i=1,j \neq i}^N (\mathbf{f}_{ij} \cdot \mathbf{r}_i + \mathbf{f}_{ji} \cdot \mathbf{r}_j) = \sum_{j,i=1,j \neq i}^N \mathbf{f}_{ij} \cdot (\mathbf{r}_i - \mathbf{r}_j)$$

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

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

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

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What to do if you cannot use the virial expression?

$$P = -\frac{\partial F}{\partial V} \underset{\Delta V \rightarrow 0}{\approx} \frac{F(V-\Delta V) - F(V)}{\Delta V}$$

$$= -k_B T \frac{\ln[Q(N, V-\Delta V, T)/Q(N, V, T)]}{\Delta V}$$

$$\text{Use: } Q(N, V, T) = \frac{V^N}{\Lambda^{3N} N!} \int ds^N \exp[-\beta U(s^N)]$$

$$P \underset{\Delta V \rightarrow 0}{=} -k_B T \frac{\ln \left\langle \left(\frac{V-\Delta V}{V} \right)^N e^{-\beta \Delta U} \right\rangle}{\Delta V}$$

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Surface tension:

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

Sample with thickness t and width W : $A = 2S = 2Wt \Rightarrow 2\lambda Wt$
 Height $H \Rightarrow H/\lambda$

Volume
 $W \times H \times t$
 Constant

Surface area
 $2S$
 changes

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

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The calculation is much the same as for the pressure, and we obtain:

$$\gamma = \frac{1}{4S} \left\langle \sum_{i=1}^N \sum_{j \neq i} [f_{ij;z} z_{ij} - f_{ij;x} x_{ij}] \right\rangle$$

This expression can be further simplified, but I will not do that.

Note: this expression does not work for solid-liquid (or solid-solid) interfaces:

$$\left(\frac{\partial F_s}{\partial A}\right) = \gamma + A \left(\frac{\partial \gamma}{\partial A}\right) \equiv t_s$$

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Heat capacity from energy fluctuations:

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

Use the Stat Mech expression for E :

$$E = - \left(\frac{\partial \ln Q}{\partial \beta} \right) = \frac{\int d\mathbf{p}^N d\mathbf{r}^N H(\mathbf{p}^N, \mathbf{r}^N) e^{-\beta H}}{\int d\mathbf{p}^N d\mathbf{r}^N e^{-\beta H}} = \langle H \rangle$$

Then it follows that:

$$C_V = \frac{1}{k_B T^2} \left(\frac{\partial^2 \ln Q}{\partial \beta^2} \right) = \frac{1}{k_B T^2} (\langle H^2 \rangle - \langle H \rangle^2)$$

In words: the heat capacity follows from the natural fluctuations in the energy

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There exist similar “fluctuation expressions” for the compressibility, for the elastic moduli of solids, for electrical and magnetic susceptibility, and much more.

However, you can also compute C_V directly from

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

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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:

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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:

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

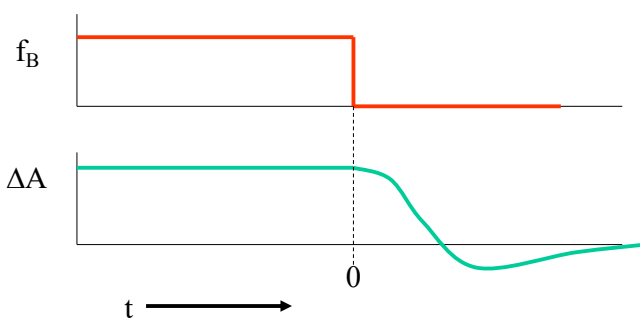
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Hence
$$\langle \Delta A \rangle \approx \beta f_B \langle BA \rangle_0$$

We can measure the “susceptibility” of an observable A , to an applied field couple to B by measuring the static correlation of A and B .

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



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

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

The time-dependent response of A to a field that is switched off at $t=0$, is determined by the *time-correlation function* of A and B

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Simple example: computing the mobility of a particle

$$B(0) = x(0) = \int_{-\infty}^0 v_x(t) dt$$

$$A(0) = v_x(0)$$

$$\langle v_x(0) \rangle = \beta f_x \int_{-\infty}^0 dt \langle v_x(t) v_x(0) \rangle$$

$$\langle v_x(0) \rangle = \beta f_x \int_0^{+\infty} dt' \langle v_x(0) v_x(t') \rangle$$

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Simple example: computing the mobility of a particle

Experiments measure mobility m

$$\langle v_x \rangle = m f_x$$

Hence:

$$m = D/k_B T = \beta \int_0^\infty dt \langle v_x(0) v_x(t) \rangle$$

(Einstein relation. [questions ?])

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Now the 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)

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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:

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

Compute mean-squared width:

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

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

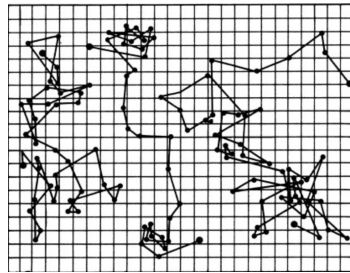


$$\frac{d \langle x^2(t) \rangle}{dt}.$$

Integrating the left-hand side by parts:

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Or:
$$2D = \lim_{t \rightarrow \infty} \frac{d \langle x^2(t) \rangle}{dt}$$



This is how Perrin measured the diffusion coefficient of Brownian particles

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

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

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

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

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

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

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

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

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

(“Green-Kubo relation”)

But we already derived this, using linear response theory (with $m = D/k_B T$)

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Illustration:

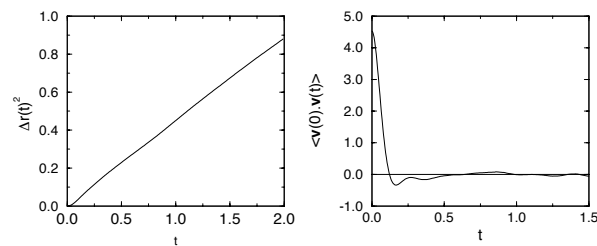


Figure 4.6: (left) Mean-squared displacement $\Delta r(t)^2$ as a function of the simulation time t . Note that for long times, $\Delta r(t)^2$ varies linearly with t . The slope is then given by $2dD$, where d is the dimensionality of the system and D the self-diffusion coefficient. (right) Velocity autocorrelation function $\langle v(0) \cdot v(t) \rangle$ as a function of the simulation time t .

WARNING: Diffusion coefficients have very large finite-size effects, which only decay as $1/N^{1/3}$

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Other examples of Green-Kubo relations:
shear viscosity

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

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

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Other example: thermal conductivity

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

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

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Note:

Neither the stress, nor the heat current are uniquely defined.

For non-pairwise additive potentials (e.g. in *ab-initio* simulations), this ambiguity becomes very important.

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Other example: electrical conductivity

$$\sigma_e = \frac{1}{Vk_B T} \int_0^\infty dt \langle j_x^{\text{el}}(0) j_x^{\text{el}}(t) \rangle$$

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

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Measurements are subject to statistical noise.

We need to know how long we must simulate to achieved the desired accuracy.

Consider an observable **A** (e.g. the pressure)

In an MD simulation of length τ , we determine a finite-time average:

$$A_\tau = \frac{1}{\tau} \int_0^\tau dt A(t)$$

We expect: the longer τ the more accurate the estimate.

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The variance in **A** is:

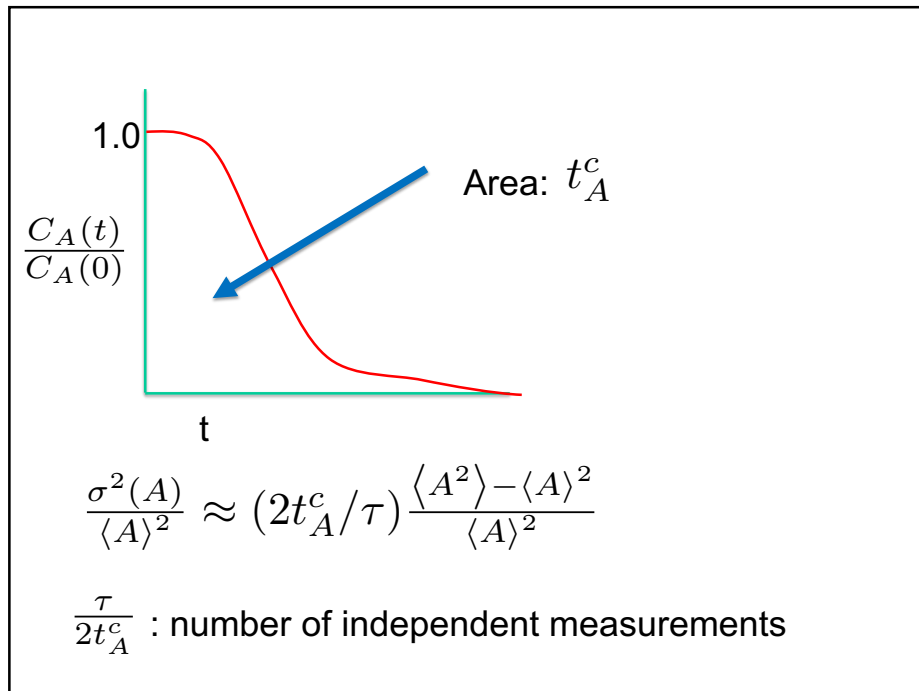
$$\sigma^2(A) = \langle A_\tau^2 \rangle - \langle A_\tau \rangle^2$$

$$= \frac{1}{\tau^2} \int_0^\tau \int_0^\tau dt dt' \langle [A(t) - \langle A \rangle] [A(t') - \langle A \rangle] \rangle$$

$$\approx \frac{1}{\tau} \int_{-\infty}^{\infty} dt C_A(t) \approx \frac{2t_A^c}{\tau} C_A(0)$$

where $2t_A^c \equiv \int_0^\infty dt \frac{C_A(t)}{C_A(0)}$

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Errors in transport coefficients

We can compute transport coefficients, using Green-Kubo relations of the form:

$$\mathcal{L}_{AA} = \lim_{t \rightarrow \infty} \int_0^t dt' \langle A(0)A(t') \rangle$$

For example, the self-diffusion coefficient is given by

$$D = \lim_{t \rightarrow \infty} \int_0^t dt' \langle v_x(0)v_x(t') \rangle$$

For definiteness, we will consider the diffusion.

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In any finite simulation, we compute:

$$D(t) = \int_0^t dt' \langle v_x(0)v_x(t') \rangle$$

It would seem that we get a better estimate of D by choosing a larger value of t

... but this is not true, because the error in $D(t)$ grows with t .

$$\sigma_{D(t)}^2 = \langle D(t)^2 \rangle - \langle D(t) \rangle^2$$

How to estimate $\sigma_{D(t)}^2$?

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

Note that:

$$\left\langle \int_0^t dt' v_x(0)v_x(t') \right\rangle^2 \approx D^2$$

That is easy. But how about:

$$\left\langle \left(\int_0^t dt' v_x(0)v_x(t') \right)^2 \right\rangle = \int_0^t dt' \int_0^t dt'' \langle v_x(0)v_x(t')v_x(0)v_x(t'') \rangle$$

We can simplify the quartic term if the fluctuations in v_x are Gaussian:

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$$\langle v_x(0)v_x(t')v_x(0)v_x(t'') \rangle \approx$$

$$\begin{aligned} & \langle v_x(0)v_x(t') \rangle \langle v_x(0)v_x(t'') \rangle + \\ & \langle v_x(0)v_x(0) \rangle \langle v_x(t')v_x(t'') \rangle + \\ & \langle v_x(0)v_x(t'') \rangle \langle v_x(0)v_x(t') \rangle \end{aligned}$$

Then, if velocity fluctuations decay on a timescale $\tau_v \ll t$:

$$\int_0^t dt' \int_0^t dt'' \langle v_x(0)v_x(t')v_x(0)v_x(t'') \rangle \approx$$

$$2D^2 + \langle v_x^2(0) \rangle (2Dt)$$

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And finally:

$$\sigma_{D(t)}^2 = \langle D(t)^2 \rangle - \langle D(t) \rangle^2 \approx$$

$$2D^2 + \langle v_x^2(0) \rangle 2Dt - D^2$$

$$D^2 + 2Dt \frac{k_B T}{m} = D^2 + 2D^2 \frac{t}{\tau_v}$$

Here τ_v is the correlation time of the velocity auto-correlation functions.

$$\frac{\sigma_{D(t)}^2}{D^2} = 1 + 2 \frac{t}{\tau_v}$$

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Note that:

$$\frac{\sigma_{D(t)}^2}{D^2} = 1 + 2\frac{t}{\tau_v}$$

applies to the case where we sample the velocity auto-correlation function only once.

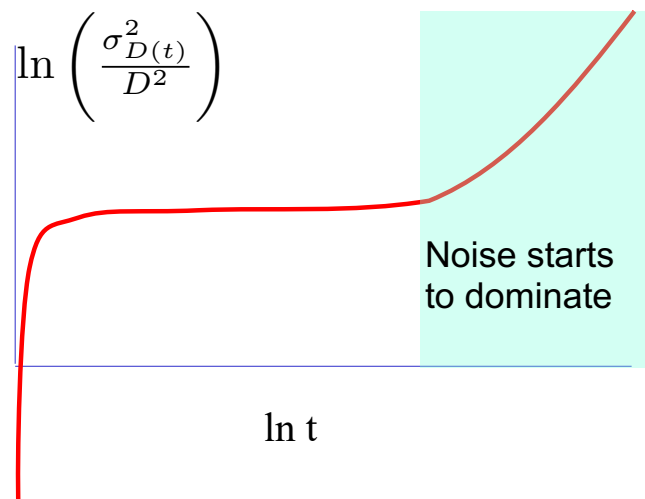
In practice, we sample many times. Typically, for a run of length t_{run} , we sample t_{run}/τ_v times.

Then

$$\frac{\sigma_{D(t)}^2}{D^2} = \frac{\tau_v}{t_{\text{run}}} + 2\frac{t}{t_{\text{run}}}$$

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Sketch:



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Finally, a general comment

Classical simulations is based on the Gibbs formulation of Statistical Mechanics (1902), i.e. before Quantum Mechanics was developed.

Gibbs never used, nor needed Planck's constant.

Therefore: **Planck's constant can *never* appear in any observable that is computed classically.**

(Question: so how about the *de Broglie* thermal wavelength Λ ?)

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Also: the indistinguishability of identical quantum particles is irrelevant for classical calculations...

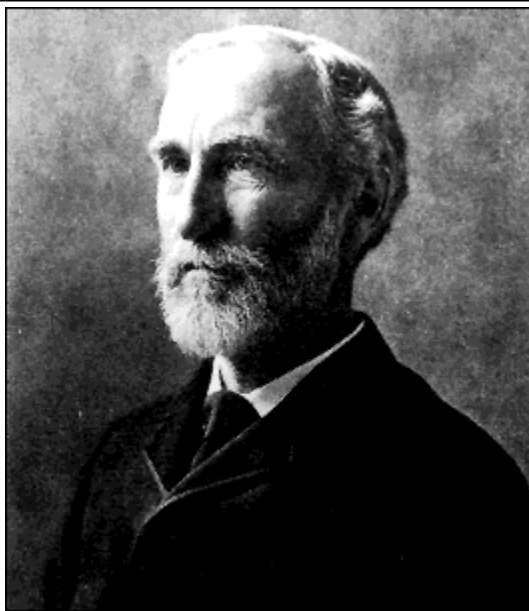
Not even for the factor $1/N!$ in the partition function?

No, not even for that.

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Where does the factor $N!$ come from?

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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 Gibbs² 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"

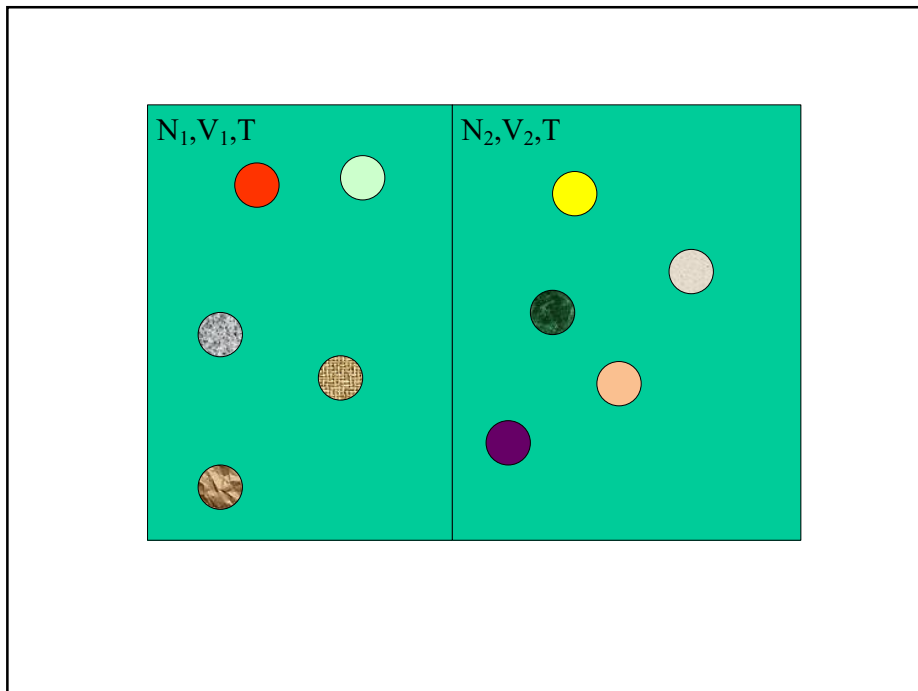
"But occasionally he delivers a sentence with a ponderous unintelligibility that seems to challenge us to make sense out of it..."

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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 labeled *but otherwise identical*

ln Z is not extensive

$$Z_{dist}(N) = V^N$$

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).

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

NOTE:

1. all particles are different (they just have identical properties – e.g. monodisperse colloidal spheres)
2. $Z_{combined}$ 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 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 ^4He 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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This was an introductory lecture to Computer Measurements.

Many of you probably knew most of it already.

However, I stressed a few points that are not widely appreciated:

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- The value of Planck's constant cannot affect the outcome of any observable that is computed classically. Hence, the value of thermal de Broglie wavelength cannot affect your results. NOTE: if a system can undergo chemical reactions, h will be important.
- The $1/N!$ has nothing to do with the quantum indistinguishability of particles.
- The use of $E_{\text{kin}} = 1/2 mv^2$ may lead to incorrect temperature estimates
- The stress and heat flux are not uniquely defined

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- Green-Kubo integrals: longer integration is not necessarily better, and often worse
- The radial distribution function of a system in equilibrium can be computed more accurately (and without binning) by using an expression based on the forces acting on particles.
- It is dangerous to compute the structure factor $S(q)$ by Fourier transforming $g(r)$
- The surface free-energy of a (structured) solid-liquid interface cannot be computed using the difference between the parallel and perpendicular components of the stress tensor.

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Thank You !

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