

Under normal circumstances, I would have
given this lecture “in real life”

...but these are not “normal circumstances”

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Computer “measurements”

1. What and what not ?
2. How ?

Daan Frenkel, U Cambridge

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

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

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

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First a general comment:

We discuss Classical simulations, based on the formulation of Statistical Mechanics in 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 an classical calculations...

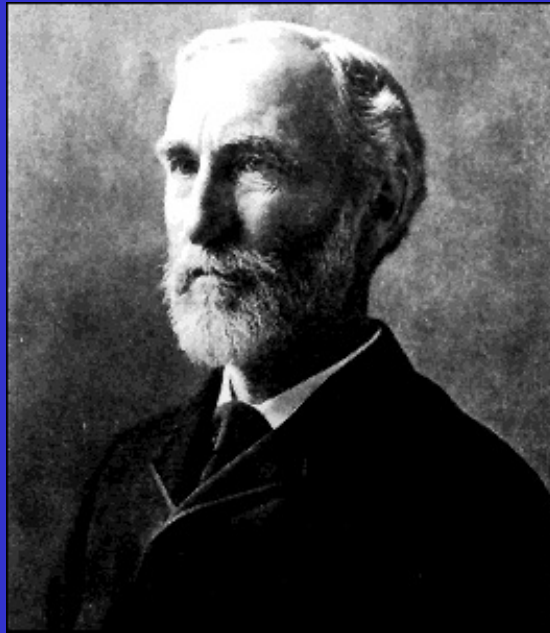
Not even for the factor $1/N!$ in the partition function?

No, not even for that.

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Where does the factor $N!$ come from?

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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 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”

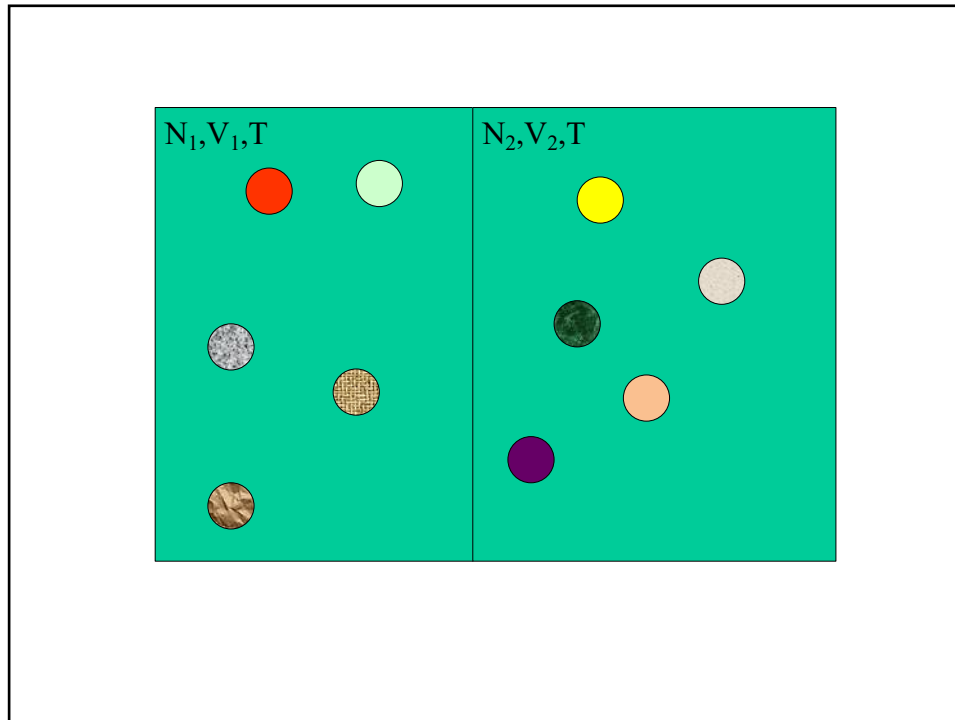
“But occasionally he delivers a sentence with a ponderous unintelligibility that seems to challenge us to make sense out of it...”

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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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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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First the easy ones

Temperature (question: how is it defined?): :

Use equipartition

Kinetic energy **K** of a system with f degrees of freedom is

$$\mathbf{K} = f (k_B T/2)$$

But what is f ?

In a closed system, $f = N d - 1$

But in a periodic system, $f = (N-1) d - 1$ (why ?)

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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:

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

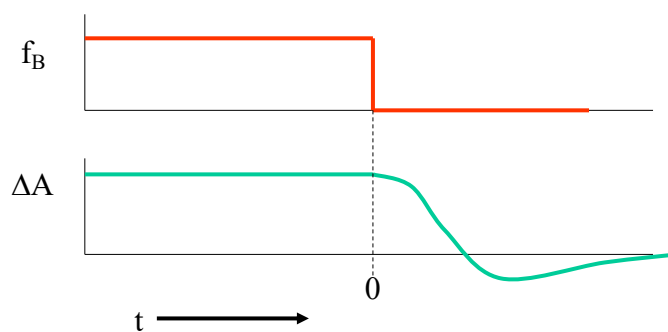
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Hence $\langle \Delta A \rangle \approx \beta f_B \langle BA \rangle_0$

We can measure the “susceptibility” of an observable A , to an applied field couple to B by measure 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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$$2D = \lim_{t \rightarrow \infty} \frac{1}{t} 2 \int_0^t dt'' \langle v_x(t - t'') v_x(0) \rangle$$

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

("Green-Kubo relation")

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

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Illustration:

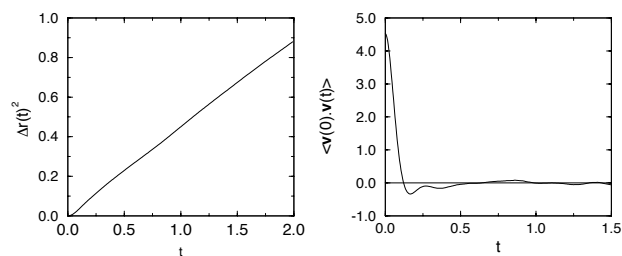


Figure 4.6: (left) Mean-squared displacement $\Delta r(t)^2$ as a function of the simulation time t . Note that for long times, $\Delta r(t)^2$ varies linearly with t . The slope is then given by $2dD$, where d is the dimensionality of the system and D the self-diffusion coefficient. (right) Velocity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

WARNING: Diffusion coefficients have very large finite-size effects (that only decay as $1/N^{1/3}$)
[question ?]

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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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Other example: electrical conductivity

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

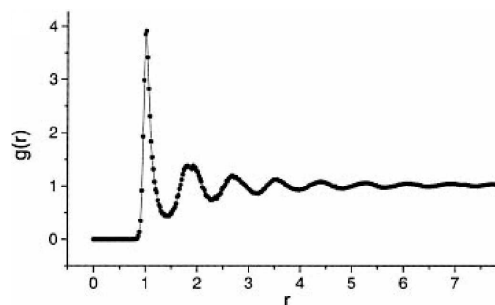
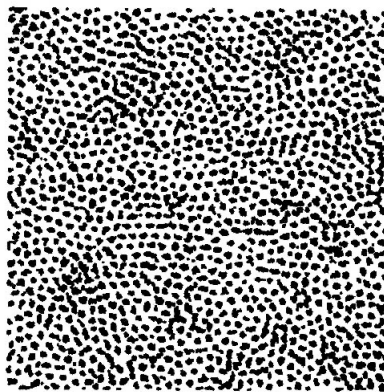
$$j_x^{\text{el}} = \sum_{i=1}^N q_i v_i^x.$$

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Sampling observable quantities:

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

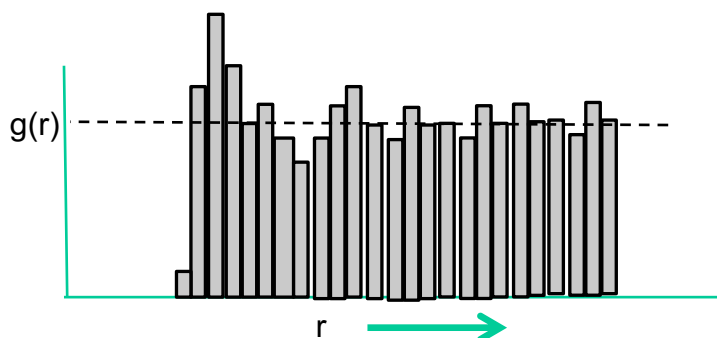
$g(r)$ = the average density at distance r from a particle, divided by the bulk density. In an ideal gas, $g(r) = 1$



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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:

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

Now, note that:

$$\delta(\mathbf{r} - \mathbf{r}_{ij}) = -\frac{1}{4\pi} \Delta_r \frac{1}{|\mathbf{r} - \mathbf{r}_{ij}|}$$

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Integrate by parts, using

$$\nabla_r = -\nabla_{r_i} = +\nabla_{r_j}$$

and

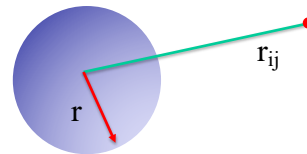
$$\nabla_{r_i} e^{-\beta U(\mathbf{r}^N)} = \beta \mathbf{F}_i e^{-\beta U(\mathbf{r}^N)}$$

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We then obtain:

$$g(r) - 1 \equiv h(r) = \frac{-\beta}{N4\pi\rho} \int d\hat{\mathbf{r}} \left\langle \sum_{i=1}^N \sum_{j \neq i}^N \frac{\mathbf{r}_{ij} - \mathbf{r}}{|\mathbf{r}_{ij} - \mathbf{r}|^3} \cdot \frac{1}{2} (\mathbf{F}_i - \mathbf{F}_j) \right\rangle$$

But $\int d\hat{\mathbf{r}} \frac{\mathbf{r}_{ij} - \mathbf{r}}{|\mathbf{r}_{ij} - \mathbf{r}|^3}$



is like the field at $\mathbf{r}_{ij}$ due to a unit charge uniformly distributed over a sphere around the origin, with radius r .

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Hence:

$$\int d\hat{\mathbf{r}} \frac{\mathbf{r}_{ij} - \mathbf{r}}{|\mathbf{r}_{ij} - \mathbf{r}|^3} = \frac{\mathbf{r}_{ij}}{r_{ij}^3} \theta(r_{ij} - r)$$

and therefore

$$h(r) = \frac{-\beta}{N4\pi\rho} \left\langle \sum_{i=1}^N \sum_{j \neq i}^N \frac{1}{2} (\mathbf{F}_i - \mathbf{F}_j) \cdot \frac{\mathbf{r}_{ij}}{r_{ij}^3} \theta(r_{ij} - r) \right\rangle$$

NOTE: we do not assume pairwise additivity

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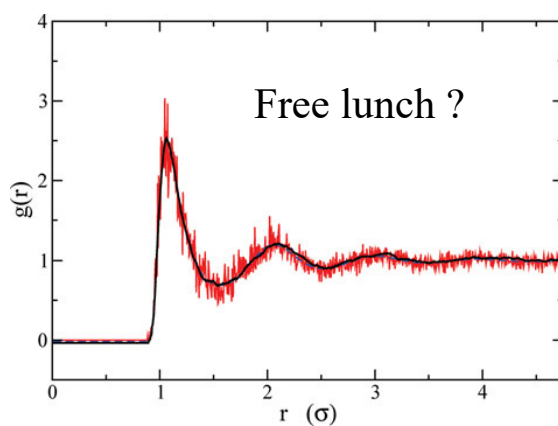


Figure 1. Radial distribution function obtained for a single equilibrated configuration of a Lennard-Jones liquid composed of 864 particles using either the force approach, Equation (6), or the standard histogram technique, with a grid spacing $\Delta r = 0.005\sigma$. The dashed blue line indicates the converged result after 10,000 simulation steps.

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More impressive: works for very short ab-initio MD runs

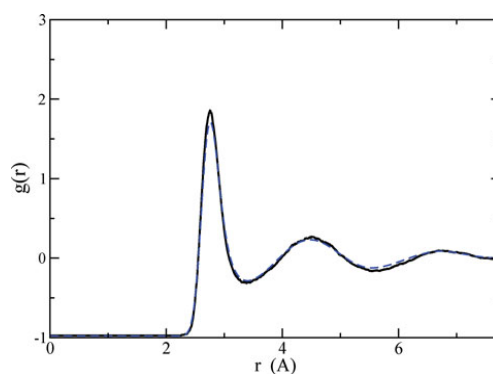


Figure 3. Oxygen-oxygen radial distribution function averaged over 100 configurations extracted from a DFT-MD trajectory with 128 water molecules at ambient liquid conditions. The dashed blue line indicates the converged result obtained by averaging over 36,800 configurations.

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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 $S(q)$

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Sampling observable
quantities:

Pressure

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1. Thermodynamic relation:

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

2. Statistical mechanical relation:

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

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:

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

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

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

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

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

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

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$$\begin{aligned}
 P &= \frac{Nk_B T}{V} \\
 &- \frac{\int d\mathbf{s}^N \sum_{i=1}^N \frac{\partial \mathcal{U}(\mathbf{r}^N)}{\partial \mathbf{r}_i} \cdot \frac{\mathbf{r}_i}{3V} \exp[-\beta \mathcal{U}(\mathbf{s}^N)]}{\int d\mathbf{s}^N \exp[-\beta \mathcal{U}(\mathbf{s}^N)]} - \left\langle \left(\frac{\partial \mathcal{U}}{\partial V} \right)_{\mathbf{s}_i} \right\rangle_{N,T} \\
 P &= \frac{Nk_B T}{V} - \left\langle \sum_{i=1}^N \frac{\partial \mathcal{U}(\mathbf{r}^N)}{\partial \mathbf{r}_i} \cdot \frac{\mathbf{r}_i}{3V} \right\rangle - \left\langle \left(\frac{\partial \mathcal{U}}{\partial V} \right)_{\mathbf{s}_i} \right\rangle_{N,T} \\
 P &= \frac{Nk_B T}{V} + \frac{1}{3V} \left\langle \sum_{i=1}^N \mathbf{f}_i \cdot \mathbf{r}_i \right\rangle - \left\langle \left(\frac{\partial \mathcal{U}}{\partial V} \right)_{\mathbf{s}_i} \right\rangle_{N,T}
 \end{aligned}$$

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$$\begin{aligned}
 P &= \frac{Nk_B T}{V} + \frac{1}{3V} \left\langle \sum_{i=1}^N \mathbf{f}_i \cdot \mathbf{r}_i \right\rangle - \left\langle \left(\frac{\partial \mathcal{U}}{\partial V} \right)_{\mathbf{s}_i} \right\rangle_{N,T} \\
 &\text{For pairwise additive forces:} \\
 \mathbf{f}_i &= \sum_{j \neq i} \mathbf{f}_{ij} \\
 &\text{Then} \\
 P &= \frac{Nk_B T}{V} + \frac{1}{3V} \left\langle \sum_{i,j=1, i \neq j}^N \mathbf{f}_{ij} \cdot \mathbf{r}_i \right\rangle
 \end{aligned}$$

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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?

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

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

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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Thank You !

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