How to compute observables

Pascal Viot

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Thermodynamics

- the mean energy $\langle E \rangle_\beta$ at the temperature $T = 1/\beta$ is obtained by calculating the integral.

$$\langle E \rangle = \int dE \, E P_\beta(E) \tag{1}$$

where $P_\beta(E)$ is the probability distribution of finding an equilibrium configuration at the temperature T.

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- In a simulation, after a period corresponding the relaxation time, the system evolves at equilibrium and the mean energy is obtained by taking the arithmetic average

$$\langle E \rangle = \frac{1}{N_c} \sum_{i=1}^{N_c} E_i \tag{2}$$

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- C_v is given by $k_b \beta^2 (\langle E^2 \rangle - \langle E \rangle^2)$

Time driven algorithm

- $$\langle A \rangle = \frac{1}{t} \sum_{0}^{t} A(t')dt' \tag{3}$$

Molecular Dynamics

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Event-driven algorithm

- $$\langle A \rangle = \frac{1}{T} \sum_{i}^{N_c} A_i t_i \tag{4}$$

where t_i is time interval between the ith and $i+1$th event (collision).

Correlation functions

Spatial correlation functions

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- Microscopic density

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- Microscopic pair density

$$\rho(\mathrm{r}, \mathrm{r}') = \sum_{i=1}^{N} \sum_{j=1, j\neq i}^{N} \delta(\mathrm{r} - \mathrm{r}_i)\delta(\mathrm{r}' - \mathrm{r}_j)$$

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- Sum rules

$$\int \overline{\rho(\mathrm{r})} d\mathrm{r} = N$$

$$\int \overline{\rho(\mathrm{r},\mathrm{r}')} d\mathrm{r} d\mathrm{r}' = N(N-1)$$

Correlation functions

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$$g(\mathrm{r},\mathrm{r}') = \frac{\rho(\mathrm{r},\mathrm{r}')}{\rho(\mathrm{r})\rho(\mathrm{r}')}.$$

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For an isotropic and homogeneous system,

$$g(\mathrm{r},\mathrm{r}) = g(|\mathrm{r}-\mathrm{r}'|)$$

Correlation functions

Implementation in a simulation.

- When the distance $|r - r'|$ is large, the radial distribution function goes to $1 - \frac{1}{N}$.

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- For an homogeneous system and homogeneous system,

$$\rho^2 g(|\mathrm{r} - \mathrm{r}'|) = \langle \sum_{i=1}^{N} \sum_{j=1, j\neq i}^{N} \delta(\mathrm{r} - \mathrm{r}_i)\delta(\mathrm{r}' - \mathrm{r}_j) \rangle$$

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Using the change of variable $\mathrm{r}, \mathrm{r}' \to \mathrm{r}, \mathrm{s} = \mathrm{r}' - \mathrm{r}$ and integrating over r

$$\rho g(s) = \frac{1}{N} \langle \sum_{i=1}^{N} \sum_{j=1, j\neq i}^{N} \delta(\mathrm{s} - \mathrm{r}_i + \mathrm{r}_j) \rangle$$

Correlation functions

Implementation in a simulation.

- In a simulation box in $3D$, space discretization of $g(r)$

$$\rho g(\Delta r(j+0.5)) = \frac{1}{N(V_{j+1}-V_j)} 2N_p(r),$$

where $N_p(r)$ is the number of distinct pairs whose center to center distances are between $j\Delta r$ and $(j+1)\Delta r$ and where $V_j = \frac{4\pi}{3}((j+1)\Delta r)^3$.

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- The maximum distance of $g(r)$ is the half of the linear size of the simulation box.

Structure factor

- Definition

$$S(\mathrm{k}) = \frac{1}{N}\langle \rho_{\mathrm{k}} \rho_{-\mathrm{k}} \rangle$$

where ρ_{k} is the Fourier transform of the microscopic density $\rho(\mathrm{r})$.

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$$S(\mathrm{k}) = 1 + \frac{1}{N}\left\langle \int\int \exp(-i\mathrm{k}(\mathrm{r}-\mathrm{r}')) \sum_{i=1}^{N} \sum_{j=1, i\neq j}^{N} \delta(\mathrm{r}-\mathrm{r}_i)\delta(\mathrm{r}-\mathrm{r}_j) d\mathrm{r} d\mathrm{r}' \right\rangle$$

which gives

$$S(\mathrm{k}) = 1 + \frac{1}{N}\int\int \exp(-i\mathrm{k}(\mathrm{r}-\mathrm{r}'))\rho(\mathrm{r},\mathrm{r}') d\mathrm{r} d\mathrm{r}'.$$

Structure factor

- For an isotropic and uniform fluid

$$S(\mathrm{k}) = 1 + \frac{\rho^2}{N} \int \int \exp(-i\mathrm{k}(\mathrm{r} - \mathrm{r}'))g(\mathrm{r}, \mathrm{r}')d\mathrm{r}d\mathrm{r}'$$

The radial distribution function only depends on $|\mathrm{r} - \mathrm{r}'|$. One then obtains

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$$S(\mathrm{k}) = 1 + \rho \int \exp(-i\mathrm{k}\mathrm{r})g(r)d\mathrm{r}.$$

- The Fourier transform only depends on the modulus $|\mathrm{k}|$

$$S(k) = 1 + 2\pi\rho \int r^2 g(r) \int_0^\pi \exp(-ikr\cos(\theta))\sin(\theta)d\theta dr$$

$$S(k) = 1 + 4\pi\rho \int_0^\infty r^2 g(r) \frac{\sin(kr)}{kr} dr.$$

Time correlation functions

- For the Ising model, one defines the spin-spin time correlation function

$$C(t) = \frac{1}{N} \sum_{i=1}^{N} < S_i(0) S_i(t) >$$

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$$C(t) = \frac{1}{N} \sum_{i=1}^{N} < S_i(0) S_i(t) >$$

- For a simple liquid made of point particles, the density autocorrelation function is

$$C(t) = \frac{1}{V} \int dr \langle \delta\rho(r, t) \delta\rho(r, 0) \rangle \tag{5}$$

where $\delta\rho(r, t)$ denotes the local density fluctuation. This autocorrelation function

Time correlation functions

Implementation

- Time average of a correlation function (or others quantities) at equilibrium uses a fundamental property of equilibrium systems, namely, time translational invariance
- in other words, if one calculates $< S_i(t')S_i(t'+t) >$, the results is independent of t'

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- $$C(t) = \frac{1}{NM} \sum_{j=1}^{M} \sum_{i=1}^{N} S_i(t_j) S_i(t_j + t).$$
- Define a timestep for $C(t)$
- Define a matrix of N_c columns and N raws (N is the total number of spins) and once equilibrated, one defines a real vector of N_c components for $C(t)$

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- $$\tau_{eq} << N_c \Delta t_c << T_{sim} \tag{6}$$

Linear response theory: results and transport coefficients

Implementation

- Consider a system at equilibrium described by the Hamiltonian $\mathcal{H}_0$. At time $t = 0$, an external force $F(t)$ is applied and the additional Hamiltonian $\mathcal{H}'$ is given by

$$\mathcal{H}' = -A(\mathrm{r}^N)F(t)$$

where $A(\mathrm{r}^N)$ is the conjugate variable .

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- $F(t) \to 0$ when $t \to \infty$
- The time evolution of the system is described by the Liouville equation

$$\begin{aligned}\frac{\partial f^{(N)}(\mathrm{r}^N, \mathrm{p}^N, t)}{\partial t} &= -i\mathcal{L}f^{(N)}(\mathrm{r}^N, \mathrm{p}^N, t) \\ &= \{\mathcal{H}_0 + \mathcal{H}', f^{(N)}(\mathrm{r}^N, \mathrm{p}^N, t)\} \\ &= -i\mathcal{L}_0 f^{(N)}(\mathrm{r}^N, \mathrm{p}^N, t) - \{A, f^{(N)}(\mathrm{r}^N, \mathrm{p}^N, t)\}F(t)\end{aligned}$$

Implementation

- Because the system was initially at equilibrium, one has

$$f^{(N)}(\mathrm{r}^N, \mathrm{p}^N, 0) = C \exp(-\beta \mathcal{H}_0(\mathrm{r}^N, \mathrm{p}^N)),$$

Implementation

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$$f^{(N)}(\mathrm{r}^N, \mathrm{p}^N, 0) = C \exp(-\beta \mathcal{H}_0(\mathrm{r}^N, \mathrm{p}^N)),$$

- Since the external force is weak, one performs a perturbative expansion of $f^{(N)}(\mathrm{r}^N)$ around equlibrium. One writes

$$f^{(N)}(\mathrm{r}^N, \mathrm{p}^N, t) = f_0^{(N)}(\mathrm{r}^N, \mathrm{p}^N) + f_1^{(N)}(\mathrm{r}^N, \mathrm{p}^N, t)$$

- $$f_1^{(N)}(\mathrm{r}^N, \mathrm{p}^N, t) = -\int_{-\infty}^{t} \exp(-i(t-s)\mathcal{L}_0)\{A, f_0^{(N)}\}F(s)ds.$$

Linear response theory: results and transport coefficients

- Therefore, the variable $\langle \Delta B(t) \rangle = \langle B(t) \rangle - \langle B(-\infty) \rangle$ evolves as

$$\langle \Delta B(t) \rangle = \int \int d\mathrm{r}^N d\mathrm{p}^N \left(f^{(N)}(\mathrm{r}^N, \mathrm{p}^N, t) - f_0^{(N)}(\mathrm{r}^N, \mathrm{p}^N) \right) B(\mathrm{r}^N) d\mathrm{r}^N d\mathrm{p}^N.$$

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$$\begin{aligned} \langle \Delta B(t) \rangle &= - \int \int d\mathrm{r}^N d\mathrm{p}^N \int_{-\infty}^{t} \exp(-i(t-s)\mathcal{L}_0) \{A, f_0^{(N)}\} B(\mathrm{r}^N) F(s) ds \\ &= - \int \int d\mathrm{r}^N d\mathrm{p}^N \int_{-\infty}^{t} \{A, f_0^{(N)}\} \exp(i(t-s)\mathcal{L}_0) B(\mathrm{r}^N) F(s) ds \end{aligned}$$

Linear response theory: results and transport coefficients

- Calculating the Poisson bracket, one obtains that

$$
\begin{aligned}
\{A, f_0^{(N)}\} &= \sum_{i=1}^{N} \left(\frac{\partial A}{\partial \mathrm{r}_i} \frac{\partial f_0^{(N)}}{d\mathrm{p}_i} - \frac{\partial A}{\partial \mathrm{p}_i} \frac{\partial f_0^{(N)}}{d\mathrm{r}_i} \right) \\
&= -\beta \sum_{i=1}^{N} \left(\frac{\partial A}{\partial \mathrm{r}_i} \frac{\partial \mathcal{H}_0^{(N)}}{d\mathrm{p}_i} - \frac{\partial A}{\partial \mathrm{p}_i} \frac{\partial \mathcal{H}_0^{(N)}}{d\mathrm{r}_i} \right) f_0^{(N)} \\
&= -\beta i \mathcal{L}_0 A f_0^{(N)} \\
&= -\beta \frac{dA(0)}{dt} f_0^{(N)}
\end{aligned}
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Linear response theory: results and transport coefficients

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Using

$$B(\mathrm{r}^N(t)) = \exp(it\mathcal{L}_0) B(\mathrm{r}^N(0)) \tag{7}$$

$$\langle \Delta B(t) \rangle = \beta \int_{-\infty}^{t} ds \left\langle \frac{dA(0)}{dt} B(t-s) \right\rangle F(s)$$

Linear response theory: results and transport coefficients

- $$\langle \Delta B(t) \rangle = \int_{-\infty}^{\infty} ds \chi(t,s) F(s) + \mathcal{O}(F^2)$$

  where $\chi(t,s)$ is the response function

Linear response theory: results and transport coefficients

- $$\langle \Delta B(t) \rangle = \int_{-\infty}^{\infty} ds \chi(t,s) F(s) + \mathcal{O}(F^2)$$

  where $\chi(t,s)$ is the response function

- 1. $$\chi(t) = \begin{cases} -\beta \frac{d}{dt} \langle A(0) B(t) \rangle & t > 0 \\ 0 & t < 0 \end{cases}$$

  2. A system cannot respond to a perturbation before it is applied. This property is a consequence of the causality.

  $$\chi(t,s) = 0, \qquad t - s \leq 0$$

  3. The equilibrium response function is translationally invariant in time

  $$\chi(t,s) = \chi(t-s) \tag{8}$$

Linear response theory: results and transport coefficients

- When $A = B$, The autocorrelation function is

$$C_A(t) = \langle A(0)A(t)\rangle,$$

and we have

$$\chi(t) = \begin{cases} -\beta \dfrac{dC_A(t)}{dt} & t > 0 \\ 0 & t < 0 \end{cases}$$

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- By defining the linear integrated response as

$$R(t) = \int_0^t \chi(s)ds$$

The fluctuation-dissipation theorem is expressed as

$$R(t) = \begin{cases} \beta(C_A(0) - C_A(t)) & t > 0 \\ 0 & t < 0 \end{cases}$$

Space-time correlation functions

Van Hove function

- $$\rho G(\mathsf{r}, \mathsf{r}'; t) = \langle \rho(\mathsf{r}' + \mathsf{r}, t)\rho(\mathsf{r}', 0)\rangle$$

Space-time correlation functions

Van Hove function

- $$\rho G(\mathrm{r}, \mathrm{r}'; t) = \langle \rho(\mathrm{r}' + \mathrm{r}, t)\rho(\mathrm{r}', 0)\rangle$$

- This function can be expressed from the microscopic densities as

$$\rho G(\mathrm{r}, \mathrm{r}'; t) = \left\langle \sum_{i=1}^{N}\sum_{j=1}^{N} \delta(\mathrm{r}' + \mathrm{r} - \mathrm{r}_i(t))\delta(\mathrm{r} - \mathrm{r}_j(0)) \right\rangle$$

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- For a homogeneous system, $G(\mathrm{r}, \mathrm{r}'; t)$ only depends on the relative distance. Integrating over volume, one obtains

$$G(\mathrm{r}, t) = \frac{1}{N}\left\langle \sum_{i=1}^{N}\sum_{j=1}^{N} \delta(\mathrm{r} - \mathrm{r}_i(t) + \mathrm{r}_j(0)) \right\rangle$$

Space-time correlation functions

Van Hove function

- At $t = 0$, the Van Hove function $G(\mathrm{r}, t)$ is simplified and one obtains

$$G(\mathrm{r}, 0) = \frac{1}{N} \left\langle \sum_{i=1}^{N} \sum_{j=1}^{N} \delta(\mathrm{r} + \mathrm{r}_i(0) - \mathrm{r}_j(0)) \right\rangle$$
$$= \delta(\mathrm{r}) + \rho g(\mathrm{r})$$

Space-time correlation functions

Van Hove function

- Function splitting

$$G(\mathrm{r}, t) = G_s(\mathrm{r}, t) + G_d(\mathrm{r}, t)$$

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- Physical interpretation

Space-time correlation functions

Van Hove function

- Normalization rules

$$\int dr G_s(r, t) = 1$$

Space-time correlation functions

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Space-time correlation functions

Van Hove function

- Normalization rules

$$\int dr G_s(r,t) = 1$$

- $$\int dr G_d(r,t) = N - 1$$

- In the long time limit, the system looses memory of the initial configuration and the correlation functions becomes independent of the distance r.

$$\lim_{r\to\infty} G_s(r,t) = \lim_{t\to\infty} G_s(r,t) \simeq \frac{1}{V} \simeq 0$$
$$\lim_{r\to\infty} G_d(r,t) = \lim_{t\to\infty} G_s(r,t) \simeq \frac{N-1}{V} \simeq \rho$$

Space-time correlation functions

Intermediate scattering function

- $$F(\mathrm{k},t) = \int d\mathrm{k} G(\mathrm{r},t) e^{-i\mathrm{k}.\mathrm{r}t}$$

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Intermediate scattering function

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- self part of the function

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- self part of the function
$$F_s(\mathrm{k},t) = \int d\mathrm{k} G_s(\mathrm{r},t) e^{-i\mathrm{k}\mathrm{r}t}$$
- distinct part of the function
$$F_d(\mathrm{k},t) = \int d\mathrm{k} G_d(\mathrm{r},t) e^{-i\mathrm{k}\mathrm{r}t}$$

Space-time correlation functions

Dynamic structure factor

- $$S(\mathrm{k},\omega) = \int dt F(\mathrm{k},t) e^{i\omega t}$$

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Space-time correlation functions

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- To be continued... $4-$point correlation function, point-to-set function...