Thermodynamic properties

In MD, a trajectory is represented by

$$\left[\vec{r}^{\,N}(k\Delta t), \vec{p}^{\,N}(k\Delta t)\right] \qquad k = 1, \dots, M$$

Δt : time-step

$$\Rightarrow \langle A \rangle = \frac{1}{M} \sum_{k=1}^{M} A\left[\vec{r}^{\,N}(k\Delta t)\ \vec{p}^{\,N}(k\Delta t)\right]$$

Energy

$$E = \mathcal{H}(\vec{r}^{\,N}, \vec{p}^{\,N}) = \text{const}$$

$$E = E_K + U$$

$$\langle E_K \rangle = \frac{3}{2} N k_B T = \frac{1}{\sum_{i=1}^{N} 2m_i} \frac{1}{M} \sum_{k=1}^{M} \sum_{i=1}^{N} p_i^2(k\Delta t)$$

N # particles

$$\langle U \rangle = \frac{1}{M} \sum_{k=1}^{M} \sum_{i<j} u_p\left[\vec{r}_{ij}(k\Delta t)\right]$$

Pressure

$$P = \rho k_B T - \frac{1}{3V} \left\langle \sum_{i<j} \vec{r}_{ij} \frac{d u_p(r_{ij})}{d r_{ij}} \right\rangle$$

lut620.pdb =====>clb606.pdb

car 1 574.33 nm -> chl

	Uda	Ud-d	Rcc
1 650.12 nm	-9.4	-1.7	28.1
2 636.78 nm	2.1	0.4	28.1
3 620.74 nm	1.2	0.6	28.1
4 579.20 nm	-2.1	-0.4	28.1
5 551.43 nm	2.1	0.7	28.1
6 540.20 nm	-7.4	-1.8	28.1
7 537.57 nm	-4.3	-2.0	28.1
8 515.27 nm	7.7	1.6	28.1
9 507.18 nm	1.4	0.5	28.1
10 490.93 nm	10.1	2.9	28.1
11 415.43 nm	-5.8	-1.1	28.1
12 407.58 nm	0.6	-0.6	28.1
13 403.20 nm	-6.2	-1.3	28.1
14 399.69 nm	1.2	0.5	28.1
15 385.87 nm	-0.1	-0.1	28.1
16 383.87 nm	4.5	0.3	28.1
17 382.98 nm	1.9	0.5	28.1
18 377.52 nm	-0.1	-0.6	28.1
19 375.21 nm	-8.3	-3.0	28.1
20 370.49 nm	4.9	0.6	28.1

car 2 544.45 nm -> chl

	Uda	Ud-d	Rcc
1 650.12 nm	0.4	0.0	28.1
2 636.78 nm	-0.1	0.0	28.1
3 620.74 nm	-0.1	0.0	28.1
4 579.20 nm	0.1	0.0	28.1
5 551.43 nm	0.0	0.0	28.1
6 540.20 nm	0.0	0.1	28.1
7 537.57 nm	0.0	0.1	28.1
8 515.27 nm	-0.2	0.0	28.1
9 507.18 nm	0.0	0.0	28.1
10 490.93 nm	-0.6	-0.1	28.1
11 415.43 nm	0.2	0.0	28.1
12 407.58 nm	0.1	0.0	28.1
13 403.20 nm	0.3	0.0	28.1
14 399.69 nm	-0.1	0.0	28.1
15 385.87 nm	0.0	0.0	28.1
16 383.87 nm	-0.2	0.0	28.1
17 382.98 nm	-0.2	0.0	28.1
18 377.52 nm	-0.1	0.0	28.1
19 375.21 nm	0.1	0.1	28.1
20 370.49 nm	0.1	0.0	28.1

car 3 492.11 nm -> chl

	Uda	Ud-d	Rcc
1 650.12 nm	1.8	0.2	28.1
2 636.78 nm	-0.4	-0.1	28.1
3 620.74 nm	-0.2	-0.1	28.1
4 579.20 nm	0.4	0.1	28.1
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9 507.18 nm	-0.2	-0.1	28.1
10 490.93 nm	-2.0	-0.4	28.1
11 415.43 nm	1.0	0.2	28.1
12 407.58 nm	0.0	0.1	28.1
13 403.20 nm	1.2	0.2	28.1
14 399.69 nm	-0.4	-0.1	28.1
15 385.87 nm	0.0	0.0	28.1

Time correlation function

Two signals $A(t)$, $B(t)$

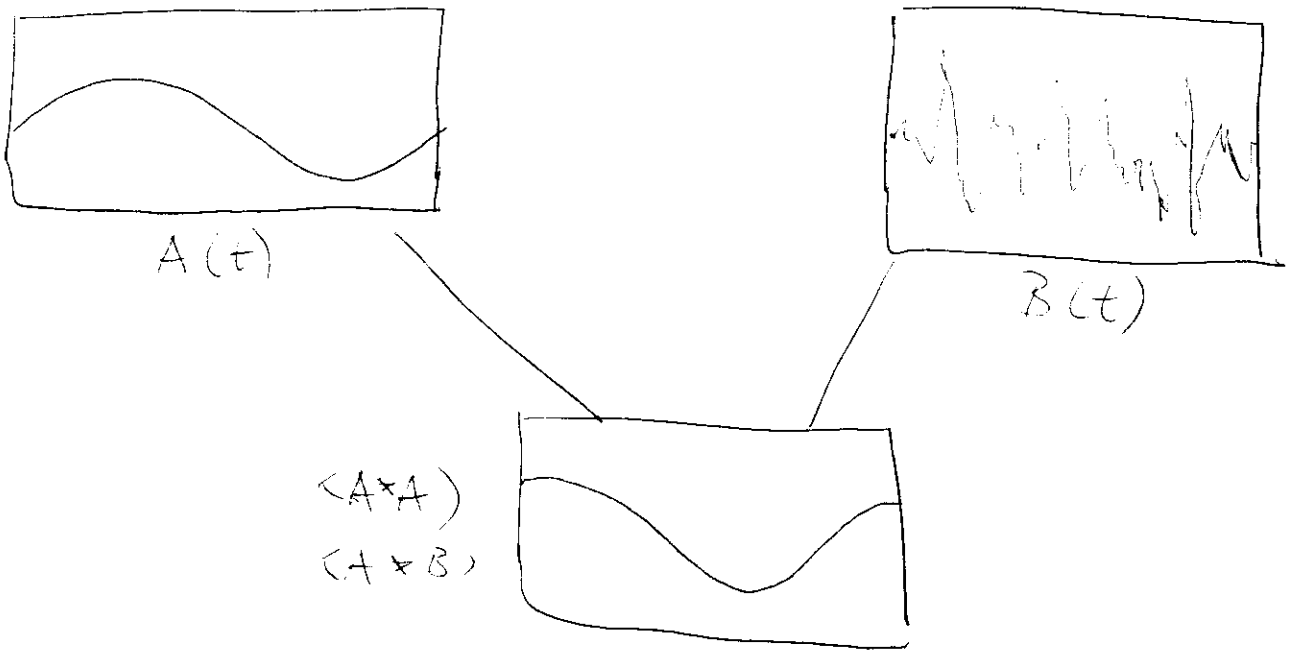
TCF $C(t) = \lim_{\tau \to \infty} \frac{1}{\tau} \int_0^{\tau} A(t_0)\, B(t_0 + t)\, dt_0$

average over many time origins t_0 from a system at equilibrium
(can be taken from one trajectory)
as it is independent of time origin)

short form $C(t) = \langle A(t_0)\, B(t_0 + t) \rangle$

If A and B are uncorrelated, then
$C \to \langle A \rangle \langle B \rangle$

$A \neq B$: cross - correlation.
$A = B$: auto - correlation.



16	383.87 nm	-0.9	0.0	28.1
17	382.98 nm	-0.5	-0.1	28.1
18	377.52 nm	-0.1	0.1	28.1
19	375.21 nm	1.3	0.4	28.1
20	370.49 nm	-0.6	-0.1	28.1

If $B(t)$ is just $A(t)$ + random noise centered around 0,

$$B(t) = A(t) + R(t)$$

then

$$\langle A(t_0)\, B(t_0+t)\rangle = \langle A(t_0)\, A(t_0+t)\rangle$$

C is invariant under translations of origin.

$$\langle A(t_0)\, B(t_0+t)\rangle = \langle A(t_0+s)\, B(t_0+s+t)\rangle$$

also for $s = -t$ time reversal

$$\langle A(t_0)\, B(t_0+t)\rangle = \langle A(t_0-t)\, B(t_0)\rangle$$

i.e. $C(t)$ is an even function

$\Rightarrow$ sampling from one trajectory enough (smart way)

Why should we care?

$$P(x,t) = \frac{P_0}{2\sqrt{\pi D t}}\, e^{-\frac{x^2}{4Dt}}$$

$$\boxed{\langle [x(t) - x(0)]^2 \rangle = \frac{1}{P_0} \int x^2\, P(x,t)\, dx = 2Dt}$$

$$\lim_{t\to\infty} \frac{\langle [r(t) - r(0)]^2 \rangle}{6t} = D$$

lut620.pdb =====>clb605.pdb

car 1 574.33 nm -> chl

		Uda	Ud-d	Rcc
1	650.12 nm	-9.4	-1.7	28.1
2	636.78 nm	2.1	0.4	28.1
3	620.74 nm	1.2	0.6	28.1
4	579.20 nm	-2.1	-0.4	28.1
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12	407.58 nm	0.6	-0.6	28.1
13	403.20 nm	-6.2	-1.3	28.1
14	399.69 nm	1.2	0.5	28.1
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19	375.21 nm	-8.3	-3.0	28.1
20	370.49 nm	4.9	0.6	28.1

car 2 544.45 nm -> chl

		Uda	Ud-d	Rcc
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4	579.20 nm	0.1	0.0	28.1
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6	540.20 nm	0.0	0.1	28.1
7	537.57 nm	0.0	0.1	28.1
8	515.27 nm	-0.2	0.0	28.1
9	507.18 nm	0.0	0.0	28.1
10	490.93 nm	-0.6	-0.1	28.1
11	415.43 nm	0.2	0.0	28.1
12	407.58 nm	0.1	0.0	28.1
13	403.20 nm	0.3	0.0	28.1
14	399.69 nm	-0.1	0.0	28.1
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16	383.87 nm	-0.2	0.0	28.1
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18	377.52 nm	-0.1	0.0	28.1
19	375.21 nm	0.1	0.1	28.1
20	370.49 nm	0.1	0.0	28.1

car 3 492.11 nm -> chl

		Uda	Ud-d	Rcc
1	650.12 nm	1.8	0.2	28.1
2	636.78 nm	-0.4	-0.1	28.1
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12	407.58 nm	0.0	0.1	28.1
13	403.20 nm	1.2	0.2	28.1
14	399.69 nm	-0.4	-0.1	28.1
15	385.87 nm	0.0	0.0	28.1

Relationship between
mean-square displacement of a dynamic quantity
and macroscopic transport coefficient

(1) Each ensemble average (msd) displacement
can be replaced by a time correlation function.

$A(t)$ dynamic quantity (e.g. $x(t)$)

$$\dot{A}(t) = \frac{dA}{dt}$$

$$A(t) - A(0) = \int_0^t dt' \, \dot{A}(t')$$

$$msd = \langle [A(t) - A(0)]^2 \rangle = \int_0^t dt'' \int_0^t dt' \, \langle \dot{A}(t') \dot{A}(t'') \rangle$$

Integration over square can be changed into
2× int over only the square

$$msd = 2 \int_0^t dt'' \int_0^{t''} dt' \, \langle \dot{A}(t) \dot{A}(t'') \rangle$$

$$\tau = t'' - t' \qquad dt' = -d\tau$$

$$= -2 \int_0^t dt'' \int_0^0 d\tau \, \langle \dot{A}(\tau) \dot{A}(0) \rangle$$

$$= 2 \int_0^t dt'' \int_0^{t''} d\tau \, \langle \dot{A}(\tau) \dot{A}(0) \rangle$$

Integration can be exchanged

16	383.87 nm	4.3	0.0	21.5
17	382.98 nm	3.1	0.5	21.5
18	377.52 nm	0.6	0.0	21.5
19	375.21 nm	-2.4	-0.7	21.5
20	370.49 nm	1.5	-0.1	21.5

$$\therefore sd = 2 \int_0^t d\tau \langle A(\tau) A(0) \rangle \int_\tau^t dt''$$

$$= 2t \int_0^t d\tau \langle A(\tau) A(0) \rangle \left(1 - \frac{\tau}{t}\right)$$

$$\frac{\langle [A(t) - A(0)]^2 \rangle}{2t} = \int_0^t d\tau \langle A(\tau) A(0) \rangle \left(1 - \frac{\tau}{t}\right)$$

$t \to \infty$

$$\boxed{\lim_{t \to \infty} \frac{\langle [A(t) - A(0)]^2 \rangle}{2t} = \int_0^\infty dt \langle A(\tau) A(0) \rangle}$$

Kubo - Green relationship

lut620.pdb ====>clb601.pdb

car 1 574.33 nm -> chl

		Uda	Ud-d	Rcc
1	650.12 nm	4.5	3.3	21.5
2	636.78 nm	4.0	0.6	21.5
3	620.74 nm	-0.2	0.4	21.5
4	579.20 nm	5.5	2.2	21.5
5	551.43 nm	-2.2	-1.4	21.5
6	540.20 nm	-3.4	5.1	21.5
7	537.57 nm	0.0	1.1	21.5
8	515.27 nm	-0.8	-2.9	21.5
9	507.18 nm	-0.9	-0.5	21.5
10	490.93 nm	-27.0	-9.7	21.5
11	415.43 nm	5.1	1.9	21.5
12	407.58 nm	12.4	2.4	21.5
13	403.20 nm	6.8	4.5	21.5
14	399.69 nm	-8.9	-2.1	21.5
15	385.87 nm	-2.8	-1.9	21.5
16	383.87 nm	-2.4	-0.2	21.5
17	382.98 nm	-15.1	-3.4	21.5
18	377.52 nm	-3.3	0.1	21.5
19	375.21 nm	4.6	4.7	21.5
20	370.49 nm	12.2	0.5	21.5

car 2 544.45 nm -> chl

		Uda	Ud-d	Rcc
1	650.12 nm	-1.7	-0.1	21.5
2	636.78 nm	0.5	0.0	21.5
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16	383.87 nm	0.9	0.0	21.5
17	382.98 nm	0.0	0.1	21.5
18	377.52 nm	-0.1	0.0	21.5
19	375.21 nm	-1.1	-0.2	21.5
20	370.49 nm	1.3	0.0	21.5

car 3 492.11 nm -> chl

		Uda	Ud-d	Rcc
1	650.12 nm	-5.7	-0.5	21.5
2	636.78 nm	0.4	-0.1	21.5
3	620.74 nm	0.8	-0.1	21.5
4	579.20 nm	-1.5	-0.3	21.5
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