Linear response

W.J. Briels

I. Linear response

A. Non-equilibrium pdf's

Generalize probability distributions in configuration space to become time dependent

$$\Pr(\vec{r}_1 \le \vec{R}_1(t) \le \vec{r}_1 + d\vec{r}_1, .., \vec{r}_N \le \vec{R}_N(t) \le \vec{r}_N + d\vec{r}_N) = P(r^{3N};t)d^{3N}r$$

Time dependence results from

$$\vec{R}_n(0) \to \vec{R}_n(t) \quad \forall n$$

Time dependent properties

$$\langle B \rangle(t) = \int dr^{3N} B(r^{3N}) P(r^{3N};t)$$

I. Linear response

A. Non-equilibrium pdf's

Notation

$$P(r^{3N};t) = \int d^{3N}x G(r^{3N}, x^{3N};\tau) P(x^{3N};t-\tau)$$

At equilibrium

$$P_{eq}(r^{3N};t) = P_{eq}(r^{3N}) = \frac{e^{-\Phi(r^{3N})/k_B T}}{Z}$$

$$P_{eq}(r^{3N}) = \int d^{3N}x G(r^{3N}, x^{3N};\tau) P_{eq}(x^{3N})$$

I. Linear response

B. Relaxation

- **Prepare system**

$$\Phi_A(r^{3N};t) = \Phi(r^{3N}) - A(r^{3N})\Theta(-t)$$

$$\rightarrow \boxed{\begin{aligned} P_A(r^{3N};0) &= \frac{e^{-\beta\Phi(r^{3N})+\beta A(r^{3N})}}{Z_A} \\ Z_A &= \int d^{3N}r e^{-\beta\Phi(r^{3N})+\beta A(r^{3N})} \end{aligned}}$$

I. Linear response

B. Relaxation

- **Prepare system**

First order in perturbation

$$Z_A = Z\left[1 + \beta\langle A\rangle\right]$$

$$Z_A^{-1} = Z^{-1}\left[1 - \beta\langle A\rangle\right]$$

$$P_A(r^{3N};0) = \frac{1}{Z}\left[1 - \beta\langle A\rangle\right]e^{-\beta\Phi(r^{3N})}\left[1 + \beta A(r^{3N})\right]$$

$$P_A(r^{3N};0) = P_{eq}(r^{3N})\left[1 + \beta\left(A(r^{3N}) - \langle A\rangle\right)\right]$$

I. Linear response

B. Relaxation

- **Average value of quantity B at time t**

$$\langle B \rangle_A(t) = \int dr^{3N} B(r^{3N}) P(r^{3N};t)$$

$$P(r^{3N};t) = \int d^{3N}x G(r^{3N}, x^{3N};t) P_{eq}(x^{3N}) \left[1 + \beta\left(A(x^{3N}) - \langle A \rangle\right)\right]$$

$$\rightarrow$$

$$\langle B \rangle_A(t) = \int d^{3N}r B(r^{3N}) \int d^{3N}x G(r^{3N}, x^{3N};t) P_{eq}(x^{3N}) \left[1 + \beta\left(A(x^{3N}) - \langle A \rangle\right)\right]$$

$$= \left(1 - \beta\langle A \rangle\right) \int d^{3N}r B(r^{3N}) \int d^{3N}x G(r^{3N}, x^{3N};t) P_{eq}(x^{3N})$$

$$+ \beta \int d^{3N}r B(r^{3N}) \int d^{3N}x G(r^{3N}, x^{3N};t) P_{eq}(x^{3N}) A(x^{3N})$$

I. Linear response

B. Relaxation

- **Average value of quantity B at time t**

$$\langle B \rangle_A (t) = \left(1 - \beta \langle A \rangle\right) \langle B \rangle + \beta \langle B(t) A(0) \rangle$$

$$\langle B(t) A(0) \rangle = \int d^{3N}x \int d^{3N}r B(r^{3N}) G(r^{3N}, x^{3N}; t) A(x^{3N}) P_{eq}(x^{3N})$$

Time correllation function!

Final result

$$\langle B \rangle_A (t) = \langle B \rangle + \beta \left[\langle B(t) A(0) \rangle - \langle B \rangle \langle A \rangle \right]$$

I. Linear response

B. Relaxation

- **Response function**

General

$$H_A(r^{3N}, p^{3N}; t) = H(r^{3N}, p^{3N}) - A(r^{3N})F(t)$$

$$\langle B \rangle_A(t) = \langle B \rangle + \int_{-\infty}^{t} dt' \Phi_{BA}(t-t')F(t')$$

Causality!!

Present case

$$\langle B \rangle_A(t) = \langle B \rangle + \int_{-\infty}^{t} dt' \Phi_{BA}(t-t')\Theta(-t')$$

I. Linear response

B. Relaxation

- **Response function**

So

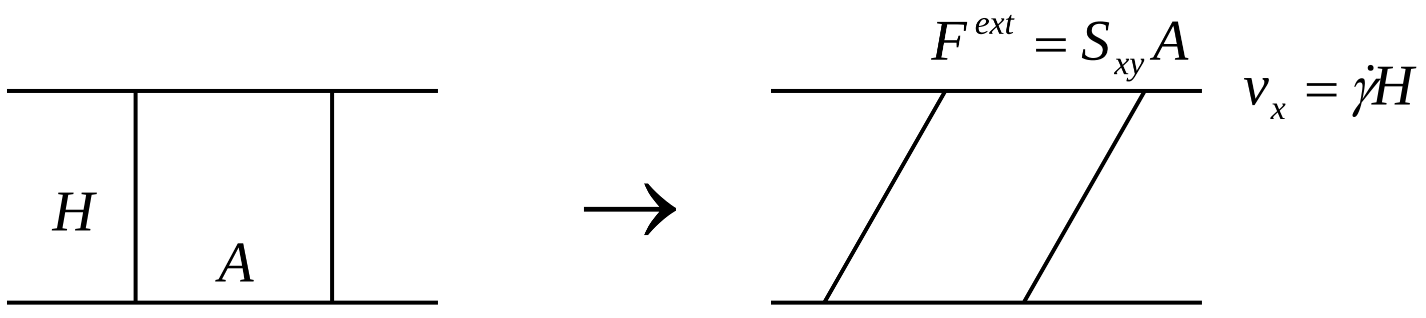
$$\int_{-\infty}^{0} dt' \Phi_{BA}(t-t') = \beta\left[\langle B(t)A(0)\rangle - \langle B\rangle\langle A\rangle\right]$$

$$\int_{t}^{\infty} dt' \Phi_{BA}(t') = \beta\left[\langle B(t)A(0)\rangle - \langle B\rangle\langle A\rangle\right]$$

$$\boxed{\Phi_{BA}(t) = -\beta \frac{d}{dt}\left[\langle B(t)A(0)\rangle - \langle B\rangle\langle A\rangle\right]}$$

II. Example: shear relaxation

A. Shear relaxation modulus



Sress

$$S_{xy}(t) = \int_{-\infty}^{t} dt' G(t - t') \dot{\gamma}(t')$$

Shear relaxation modulus: $G(t)$

II. Example: shear relaxation

A. Shear relaxation modulus

Special cases

- **Step strain** $\dot{\gamma}(t) = \gamma_0 \delta(t)$

$$\gamma(t) = \gamma_0 \Theta(t)$$

$$S_{xy}(t) = \gamma_0 \int_{-\infty}^{t} dt' G(t-t') \delta(t') = \gamma_0 G(t)$$

- **Step strain rate** $\dot{\gamma}(t) = \dot{\gamma} \Theta(t)$

$$S_{xy}(t) = \dot{\gamma} \int_{-\infty}^{t} dt' G(t-t') \Theta(t') = \dot{\gamma} \int_{0}^{t} dt' G(t')$$

$$\eta = \lim_{t \to \infty} \frac{S_{xy}(t)}{\dot{\gamma}} = \int_{0}^{\infty} dt' G(t)$$

II. Example: shear relaxation

A. Shear relaxation modulus

- **Oscillatory shear** $\dot{\gamma}(t) = \omega\gamma_0 \cos(\omega t)$

$$\gamma(t) = \gamma_0 \sin(\omega t)$$

$$S_{xy}(t) = \gamma_0 \left[G'(\omega)\sin(\omega t) + G''(\omega)\cos(\omega t) \right]$$

$$G'(\omega) = \omega \int_0^\infty dt G(t) \sin(\omega t)$$

$$G''(\omega) = \omega \int_0^\infty dt G(t) \cos(\omega t)$$

II. Example: shear relaxation

A. Shear relaxation modulus

- **Oscillatory shear details**

$$S_{xy}(t) = \int_{-\infty}^{t} dt' G(t-t')\dot{\gamma}(t')$$

$$S_{xy}(t) = \omega\gamma_0 \int_{-\infty}^{t} dt' G(t-t')\cos(\omega t')$$

Causality = upper integration limit

$$S_{xy}(t) = \omega\gamma_0 \int_{0}^{\infty} dt'' G(t'')\cos(\omega(t-t''))$$

Causality = lower integration limit

$$S_{xy}(t) = \omega\gamma_0 \int_{0}^{\infty} dt'' G(t'')\left[\cos(\omega t)\cos(\omega t'') + \sin(\omega t)\sin(\omega t'')\right]$$

I. Some macroscopic rheology

B. Kramers-Kronig

Mathematics (put in convergence factors when needed)

$$G'(\omega) = \omega \int_0^\infty dt G(t) \sin(\omega t)$$

$$G''(\omega) = \omega \int_0^\infty dt G(t) \cos(\omega t)$$

$$\rightarrow$$

$$G(t) = \frac{2}{\pi} \int_0^\infty d\omega \frac{G'(\omega)}{\omega} \sin(\omega t)$$

$$G(t) = \frac{2}{\pi} \int_0^\infty d\omega \frac{G''(\omega)}{\omega} \cos(\omega t)$$

$$G''(\omega) = \omega \int_0^\infty dt \frac{2}{\pi} \int_0^\infty d\omega' \frac{G'(\omega')}{\omega'} \sin(\omega' t) \cos(\omega t) = \omega \frac{2}{\pi} \int_0^\infty d\omega' \frac{G'(\omega')}{\omega'} \int_0^\infty dt' \sin(\omega' t) \cos(\omega t)$$

$$\rightarrow \quad \boxed{G'' = \omega \frac{2}{\pi} \int_0^\infty d\omega' \frac{G'(\omega')}{(\omega')^2 - \omega^2}}$$

II. Example: shear relaxation

C. Dissipation

Work performed per second by external force

$$F^{ext}\frac{ds}{dt} = AS_{xy}H\dot{\gamma}$$

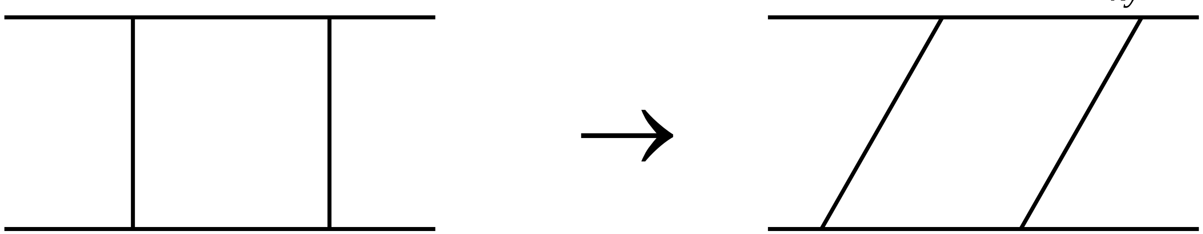
Average work performed per cycle

$$\frac{V}{2\pi/\omega}\int_0^{2\pi/\omega} dt S_{xy}(t)\dot{\gamma}(t) = V\frac{\omega\gamma_0^2}{2}G''(\omega)$$

II. Example: shear relaxation

C. Green-Kubo expression

$$F^{ext} = S_{xy} A \qquad ds = \gamma_0 H$$



Work performed by external force during step strain

$$w = F^{ext} ds = S_{xy} A \gamma_0 H$$

$$w = \Phi(\vec{r}_1 + \gamma_0 y_1 \hat{e}_x, \ldots, \vec{r}_N + \gamma_0 y_N \hat{e}_x) - \Phi(r^{3N}) \rightarrow \boxed{S_{xy} = -\frac{1}{V} \sum_n F_{x,n} y_n}$$

$$= \sum_n \frac{\partial \Phi}{\partial x_n} \gamma_0 y_n = -\gamma_0 \sum_n F_{x,n} y_n$$

II. Example: shear relaxation

C. Green-Kubo expression

Probability distribution after step strain

$$P(r^{3N},0) = P_{eq}(\vec{r}_1 - \gamma_0 y_1 \hat{e}_x, \ldots, \vec{r}_N - \gamma_0 y_N \hat{e}_x)$$

$$P(r^{3N},0) = \frac{1}{Z} e^{-\beta\Phi(r^{3N}) - \beta\gamma_0 \sum_n F_{x,n} y_n}$$

$$P(r^{3N},0) = P_{eq}(r^{3N}) e^{+\beta\gamma_0 V S_{xy}}$$

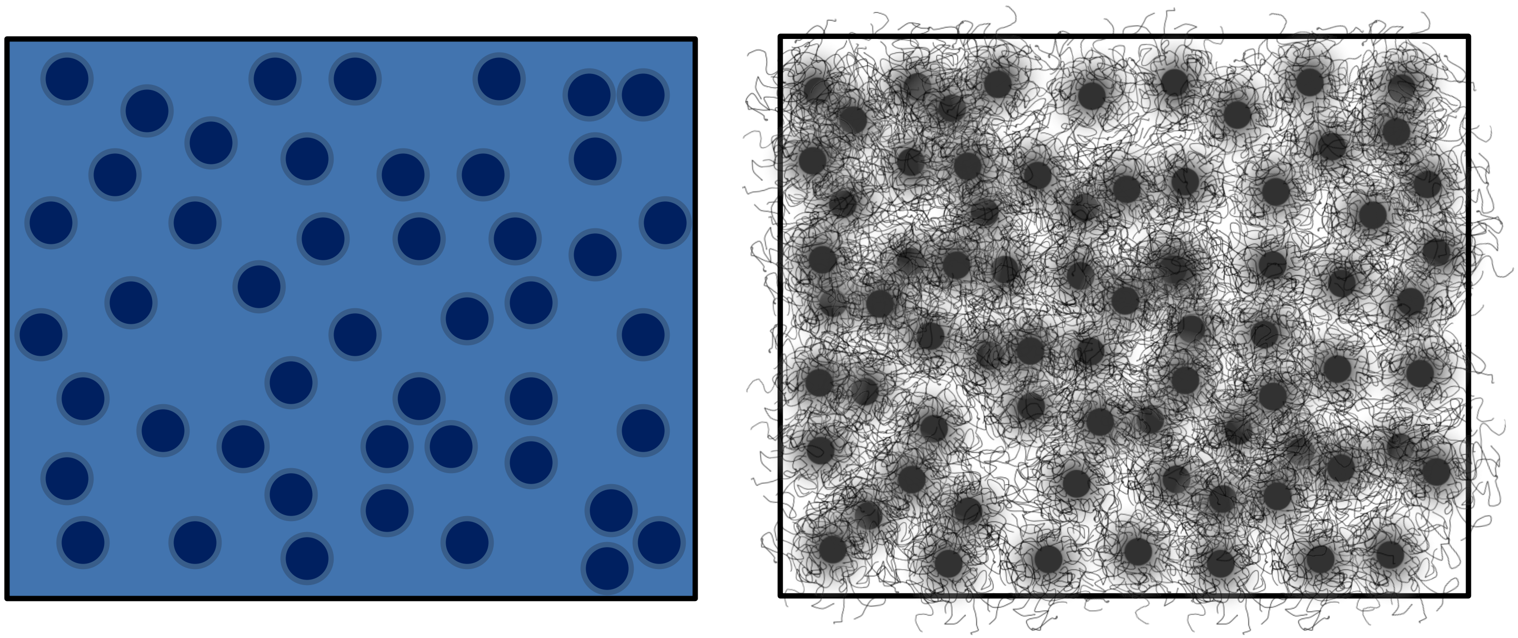
$$P(r^{3N},0) = P_{eq}(r^{3N})(1 + \beta\gamma_0 V S_{xy})$$

Shear relaxation modulus

$$G(t) = \frac{\langle S_{xy} \rangle (t)}{\gamma_0} \quad \rightarrow \quad \boxed{G(t) = \frac{V}{k_B T} \langle S_{xy}(t) S_{xy}(0) \rangle}$$

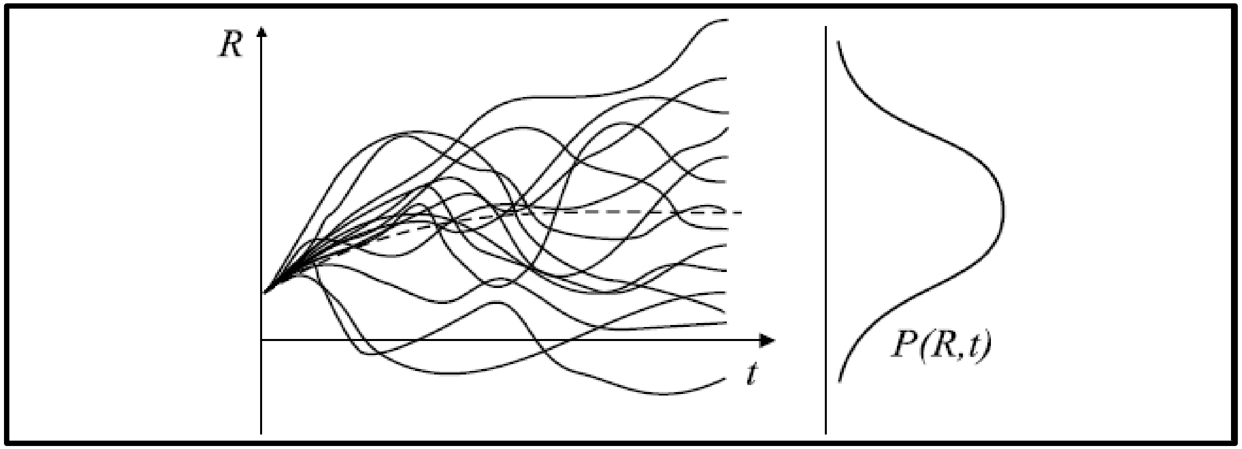
III. Coarse graining

Experimentally: limited resolution
Simulationally: limited computing power
Conceptionally: enlarged understanding



III. Coarse graining

Consider a particle with given initial position and initial velocity. Plot its path for different initial configurations and velocities of the bath



At time t you will get a distribution of positions and velocities

III. Coarse Graining

- **Full simulation using** $V(R,q)$

$$\rightarrow \qquad P(R,q) \propto e^{-\beta V(R,q)}$$

$$P(R) \propto \int d^M q e^{-\beta V(R,q)} = e^{-\beta \Phi(R)}$$

- **Coarse simulation using** $\Phi(R)$

$$\rightarrow \qquad P(R) \propto e^{-\beta \Phi(R)}$$

III. Coarse Graining

Potential of mean force

$$\Phi(R) = -k_B T \ln \int d^M q e^{-\beta V(R,q)}$$

$$\rightarrow \quad -\frac{\partial \Phi}{\partial R_n} = \frac{\int d^M q \left(-\frac{\partial V}{\partial R_n} \right) e^{-\beta V(R,q)}}{\int d^M q e^{-\beta V(R,q)}} = \left\langle -\frac{\partial V}{\partial R_n} \right\rangle_B$$

III. Coarse graining

Hamiltonian mechanics

Time evolution

$$A = A(R, P, q, p)$$

$$\rightarrow \quad \frac{dA}{dt} = \frac{dR_n}{dt}\frac{\partial A}{\partial R_n} + \frac{dP_n}{dt}\frac{\partial A}{\partial P_n} + \frac{dq_m}{dt}\frac{\partial A}{\partial q_m} + \frac{dp_m}{dt}\frac{\partial A}{\partial p_m}$$

$$= \frac{\partial H}{\partial P_n}\frac{\partial A}{\partial R_n} - \frac{\partial H}{\partial R_n}\frac{\partial A}{\partial P_n} + \frac{\partial H}{\partial p_m}\frac{\partial A}{\partial q_m} - \frac{\partial H}{\partial q_m}\frac{\partial A}{\partial p_m} \equiv i\widehat{L}A$$

III. Coarse graining

Hamiltonian mechanics

Formal solution (Taylor-expansion)

$$A(t) = \sum_{k=0}^{\infty} \frac{t^k}{k!} \frac{d^k}{dt^k} A(t)\Big|_{t=0} = \sum_{k=0}^{\infty} \frac{t^k}{k!} (i\widehat{L})^k A = e^{i\widehat{L}t} A$$

$$\frac{dA}{dt}(t) = e^{i\widehat{L}t} i\widehat{L} A$$

III. Coarse graining

Coarse equation of motion

$$\frac{dP_n}{dt}(t) = e^{i\hat{L}t} i\hat{L} P_n$$

$$\frac{dP_n}{dt}(t) = e^{i\hat{L}t}\left(-\frac{\partial V}{\partial R_n}\right) = -\frac{\partial V}{\partial R_n}(t) \equiv F_n(t)$$

$$\frac{dP_n}{dt}(t) = \langle F_n \rangle_B(t) + \left(F_n(t) - \langle F_n \rangle_B(t)\right)$$

III. Coarse graining

Rest force

$$F_n(t) - \left\langle F_n \right\rangle_B (t) = e^{i\hat{L}t}\left(F_n - \left\langle F_n \right\rangle_B\right) = e^{i\hat{L}t} F_n^{\,R}$$

Properties

$$\left\langle F_n^{\,R} \right\rangle_B = \left\langle F_n - \left\langle F_n^{\,R} \right\rangle_B \right\rangle_B = 0$$

$$\left\langle e^{iLt} F_n^{\,R} \right\rangle_B \neq 0$$

III. Coarse graining

Rest force

Notation

$$\left\langle A \right\rangle_B = \wp A$$

Make use of

$$e^{i\hat{L}t} = e^{(1-\wp)i\hat{L}t} + \int_0^t d\tau e^{i\hat{L}(t-\tau)} \wp \, iL e^{(1-\wp)i\hat{L}\tau}$$

III. Coarse graining

Result so far

$$\frac{dP_n}{dt}(t) = -\left\langle \frac{\partial V}{\partial R_n} \right\rangle_B + \int_0^t d\tau e^{iL(t-\tau)} \wp iL F_{n,\tau}^R + F_{n,t}^R$$

$$F_{n,t}^R = e^{(1-\wp)iLt} F_n^R$$

$$\left\langle F_{n,t}^R \right\rangle_B = \wp e^{(1-\wp)iLt} F_n^R = 0$$

III. Coarse graining

Evaluate Liouville operator and perform some mathematical manipulations

$$\frac{dP_n}{dt}(t) = -\frac{\partial \Phi}{\partial R_n}(t) - \sum_m \int_0^t d\tau \, \frac{P_m(t-\tau)}{M} \beta \left\langle F_m^R F_{n,\tau}^R \right\rangle_B (t-\tau) + F_{n,t}^R$$

Memory !!! **Fluctuation-dissipation !!!**

Thank you

Brrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrriels