Start with Fokker-Planck equation

$$\partial_t p(x,t) = \Omega(x)\, p(x,t) \qquad x \in \{\text{configuration space}\}$$

e.g. Brownian particles: $\Omega = \sum_{k=1}^{N} \partial_k \cdot (\partial_k - F_k)$

$F_k = -\partial_k U$ potential interaction forces

[$\Omega = \sum_k \partial_k \cdot \partial_k$ would give diffusion equation for non-interacting part.]

define scalar product: for any functions f, g of the state-space variable x

$$(f, g) := \int f^*(x)\, g(x)\, dx$$

average of $f(x)$: $\langle f \rangle(t) = \int p(x,t)\, f(x)\, dx$

define <u>weighted</u> scalar product:

$$\langle f, g \rangle := \int p(x,t)\, \delta f^*(x)\, \delta g(x)\, dx$$

with $\delta f = f - \langle f \rangle \leadsto \langle \delta f \rangle = 0$ etc.

operator adjoints: define $(f, \Omega g) = (\Omega^+ f, g)$

$$\int f^*(x)\left[\Omega(x)\, g(x)\right] dx = \int \left[\Omega^+(x)\, f^*(x)\right] g(x)\, dx$$

e.g. Smoluch.: $\int f^*(x)\left[\partial\cdot(\partial - F)\, g(x)\right] dx$

$$= -\int (\partial f^*)\,(\partial - F) g\;dx$$

$$= \int\left[(\partial\cdot\partial f^*)\, g + F\,(\partial f^*)\, g\,\right] dx$$

thus $\Omega^+ = \sum_{k=1}^{N} (\partial_k + F_k)\cdot\partial_k$

define $\langle \Omega^+ f, g\rangle = \langle f, \Omega^\ddagger g\rangle$ adjoint w.r.t. weighted scalar prod.

$$\int dx\, p(x)\left[\Omega^+(x)\, f^*(x)\right] g(x)$$

$\uparrow$ assume $\langle f\rangle = 0 = \langle g\rangle$ for simplicity

$$= \int dx\, f^*(x)\left[\Omega(x)\, p(x)\, g(x)\right]$$

but $\Omega(x)\, p(x)\, g(x) = \,?$

take $p(x) \equiv p_{eq}(x) = e^{-U}$ Boltzmann distrib.

$$\partial(\partial - F)\, e^{-U} g = \partial\partial e^{-U} g - \partial F e^{-U} g$$

$$= \partial e^{-U}\partial g + \partial F e^{-U} g - \partial F e^{-U} g$$

$$= e^{-U}\partial\partial g + F\,\partial g = e^{-U}(\partial + F)\partial g$$

hence $\Omega^\ddagger \equiv \Omega^+$ for equilibrium Smoluch. eqn.

note: formal solution $p(x,t) = \exp[\Omega t]\, p(x,0)$

since $\langle f \rangle(t) = \int dx\, p(x,t)\, f(x)$

$$= \int dx\, [\exp[\Omega t]\, p(x,0)]\, f(x)$$

$$= \int dx\, p(x,0)\, \exp[\Omega^+ t]\, f(x)$$

$\rightsquigarrow$ define $f(x,t) = \exp[\Omega^+ t]\, f(x,0)$

(cf. Heisenberg / Schrödinger picture in QM)

correlation function: given a fluctuation at x' at time t', what is the probability at x at later t?

$\rightsquigarrow$ transition probability: $p(x,t\,|\,x',t')$

obeys $\partial_t p(x,t\,|\,x',t') = \Omega(x)\, p(x,t\,|\,x',t')$

(Markov process! $p(x,t|x',t')$ obeys same PDE as $p(x,t)$, but with initial cond. $p(x,t'\,|\,x',t') = \delta(x-x')$)

<u>def.</u> $C_{fg}(t,t') = \int dx \int dx'\; \delta f^*(x)\; p(x,t\,|\,x',t')\, \delta g(x')\, p(x',t')$

$$= \int dx \int dx'\; \delta f^*(x) \left[\exp[\Omega(x)(t-t')]\, \delta(x-x')\right] \delta g(x')\, p \ldots$$

$$= \int dx \int dx' \left[\exp[\Omega^+(x)(t-t')]\, \delta f(x)\right] \delta(x-x')\, g(x')\, p(x')$$

assume that $p(x,t') = p_{eq}(x)$: "transient" correlation function:

$$C_{fg}(t,t') = \int dx \left[\exp[\Omega^+(x)(t-t')]\,\delta f^*(x)\right] \delta g(x)\, p(x)$$

$$\equiv \langle e^{\Omega^+(t-t')} f, g \rangle = \text{fn. of } t-t' \text{ in steady state}$$

goal: derive equation for $C_{ff}(t)$ (set $t'=0$)

$$\partial_t f^*(x,t) = \exp[\Omega^+ t]\,\Omega^+ f^*(x,0)$$

$$= \exp[\Omega^+ t]\,(\Omega_p^+ + \Omega_q^+)\, f^*(x,0)$$

for any splitting $\Omega^+ = \Omega_p^+ + \Omega_q^+$

observe $\exp[\Omega^+ t] \neq \exp[\Omega_p^+ t]\exp[\Omega_q^+ t]$

if Ω_p^+, Ω_q^+ do not commute

but: Dyson equation

$$e^{\Omega^+ t} = e^{\Omega_q^+ t} + \int_0^t e^{\Omega^+(t-t')}\,\Omega_p^+\, e^{\Omega_q^+ t'}\, dt'$$

$$\Rightarrow \partial_t f^*(t) = e^{\Omega^+ t}\,\Omega_p^+ f^*(0) + e^{\Omega_q^+ t}\,\Omega_q^+ f^*(0)$$
$$+ \int_0^t dt'\, e^{\Omega^+ t'}\,\Omega_p^+\, e^{\Omega_q^+(t-t')}\,\Omega_q^+ f^*(0)$$

idea: let f be <u>slow</u> variable

goal: seek equation that contains all other variables ("<u>fast</u>" modes) only "hidden" away note: Scalar product defines "orthogonality"

↝ take equation for $\partial_t f^*(t)$ and look at its <u>projection</u> onto the subspace spanned by f

projection operator: $\mathcal{P} = f^*\rangle \frac{1}{\langle f, f\rangle} \langle f^*$

$$\equiv f^*(x,0) \frac{1}{\int dx\, \rho(x)\, f^*(x)\, f(x)} \int dx\, \rho(x)\, f(x)\cdot$$

operator sense!

obeys $\mathcal{P} f = f$, let $\mathcal{Q} = 1 - \mathcal{P}$

set $\Omega_p^+ = \mathcal{P}\Omega^+$, $\Omega_Q^+ = \mathcal{Q}\Omega^+$

$$\rightsquigarrow \partial_t f^*(t)\rangle = e^{\Omega^+ t} f^*\rangle \frac{1}{\langle f, f\rangle} \langle f^*, \Omega^+ f^*\rangle$$

$$+ e^{\mathcal{Q}\Omega^+\mathcal{Q} t}\, \mathcal{Q}\Omega^+ f^*\rangle$$

$$+ \int_0^t dt'\, e^{\Omega^+ t'} f^*\rangle \frac{1}{\langle f, f\rangle} \langle f^*, \Omega^+ \mathcal{Q}\, e^{\mathcal{Q}\Omega^+\mathcal{Q}(t-t')}\, \mathcal{Q}\Omega^+ f^*\rangle$$

(where we have written $f^* \equiv f^*(x,0)$
and used $\mathcal{Q}^2 = \mathcal{Q}$ to insert some $\mathcal{Q}$'s where convenient)

↝ define $\Delta := \langle f^*, \Omega^+ f^*\rangle / \langle f, f\rangle$ = some constant

$F^* := \mathcal{Q}\Omega^+ f^*$ "fluctuating force"

lives in $\mathcal{Q}$-subspace: <u>fast</u> variable

$$K(t) = \langle \mathcal{F}^*, e^{Q\Omega^+ Q(t-t')} \mathcal{F}^* \rangle / \langle f, f \rangle$$

memory function = correlation function of fluctuating forces

formed with <u>reduced dynamics</u> that is restricted to subspace $\perp f$ all the time: $Q\Omega^+ Q$ instead of Ω^+ !

$\rightsquigarrow$ generalized Langevin equation

$$\partial_t f^*(t) = \Delta f^*(t) + \mathcal{F}^*(t) + \int_0^t K(t-t') f^*(t') dt'$$

linked (c.f. FDT)

integrate with $\int dx\, p(x) f(x)$ on both sides:

$$\boxed{\partial_t C_{ff}(t) = \Delta C_{ff}(t) + \int_0^t K(t-t') C_{ff}(t') dt'}$$

Mori-Zwanzig memory equation

example: $f = \varrho(\vec{q}) = \sum_{k=1}^{N} e^{i\vec{q}\vec{r}_k}$ local density

$C_{ff} \equiv \Phi(q,t)$ (in isotropic system only depends on $q = |\vec{q}|$)

$$\Rightarrow \langle \rho, \rho \rangle \Delta = \int d\{r\}\, e^{-U} \sum_k e^{iqr_k} \sum_j \sum_\ell (\partial_\ell - F_\ell)\, \partial_\ell\, e^{-iqr_j}$$

$$= \int d\{r\}\, e^{-U} \sum_{kj\ell} e^{iqr_k} (\partial_\ell - F_\ell)(-iq)\,\delta_{j\ell}\, e^{-iqr_j}$$

$$= \int d\{r\}\, e^{-U} \sum_{kj\ell} e^{iq(r_k - r_\ell)} (-q^2 + \underbrace{iqF_\ell}_{}) \,\delta_{j\ell}$$

vanishes due to $\Sigma\{\text{all forces}\} = 0$ (actio = reactio)

$$= -q^2 \int d\{r\}\, e^{-U} \sum_{jk} e^{iq(r_k - r_j)}$$

$$=: -q^2 S(q) = -q^2 \langle \rho, \rho \rangle$$

↳ static structure factor

$\Rightarrow$ even neglecting $K(t)$ completely, we get a plausible approx. for relaxation of density fluctuations in Brownian systems at low density (ignoring long-time tails)

i.e. $\partial_t \Phi(q,t) \simeq -q^2 \Phi(q,t)$

$\hat{=}$ solution of diffusion equation

(we set $D=1$ above, $\Phi(q,t) = e^{-q^2 D t}$)

paradigm of Mori-Zwanzig:

pick out all slow variables in f

$\Rightarrow$ F, $K(t)$ are quickly decorrelating (fast)

$\Rightarrow$ try simple ansatz there, e.g. $K \equiv 0$, $K \sim \delta(t)$, etc.

paradigm of MCT:

pick out slow density mode $f \equiv \rho$

but: cage effect $\Rightarrow$ forces given by slowly changing potential energy configuration

in Smoluch. dynamics : $F^* \sim Q\Omega^+ \rho^*$

$\sim Q\,(\partial\partial + F\partial)\,\rho^*$

$\sim Q\,(-q^2 - iqF)\,\rho^*$

can be identified with local longitudinal stresses

$\rightsquigarrow$ $K(t)$ might contain slow modes

$\rightsquigarrow$ seek approximation in terms of ϕ's themselves

for technical reasons: don't approximate K, but rewrite K in the same spirit as above

($Q\Omega^+Q$ is not one-particle irreducible)

$\rightsquigarrow$ $\tau\partial_t\phi(t) + \phi(t) + \int_0^t m(t-t')\,\partial_{t'}\phi(t')\,dt' = 0$

MCT approx.: $m \equiv \mathcal{F}[\phi^2]$ schematically