Brownian Dynamics

{A+T Chapter 12 ?
Nb van Kampen, Stochastic Processes}

intuitive argument: big object in bath of small fluctuating objects

e.g. dust in air (Brown), colloidal particle / macromolecule } in liquid

$$m\ddot{\underline{r}} = \underline{F} - \gamma \dot{\underline{r}} + \underline{\eta}(t)$$

applied force ↑, friction force ↑, random force ↑

$$\begin{cases} \langle \underline{\eta}(t) \rangle = 0 \\ \langle \eta_i(t) \eta_j(t') \rangle = \Gamma \delta_{ij} \delta(t-t') \end{cases}$$

previously – $F=0$ in 1-d

$$v(t) = v(0) e^{-\gamma t/m} + \frac{1}{m}\int_0^t dt' \, e^{-\frac{\gamma}{m}(t-t')} \eta(t')$$

$$\langle v(t)^2 \rangle = \frac{kT}{m} \Rightarrow \Gamma = 2\gamma kT \quad \text{"FDT"}$$

physical origin: in time Δt

energy loss from friction $= \frac{m}{2}\left[v(t+\Delta t)^2 - v(t)^2 \right]$

$$= \frac{m}{2} v^2(0) \left[e^{-2\gamma \Delta t/m} - 1 \right]$$

$$\simeq \frac{kT}{2} \cdot \left[-2\gamma \Delta t / m \right]$$

energy gain from bath $= \frac{1}{2m}\left[(mv + \eta\sqrt{\Delta t})^2 - (mv)^2 \right]$

$$= \frac{1}{2m} \eta^2 \Delta t \quad \text{since } \langle \eta \rangle = 0$$

equate these: $\eta^2 = 2\gamma kT$

Also $\langle (x(t) - x(0))^2 \rangle \xrightarrow[t\to\infty]{} 2Dt \Rightarrow D = \frac{kT}{\gamma}$ Stokes Einstein derivation: $x(t) - x(0) = \int_0^t dt' \, v(t')$

$+ \quad \frac{d}{dt} \langle (x(t) - x(0))^2 \rangle = 2 \langle (x(t) - x(0)) \, v(t) \rangle$

substitute → triple integral → ...

General derivation:

total particle flux $\underline{j} = \mu \rho \underline{F} - D \frac{\partial \rho}{\partial \underline{r}}$

mobility $= \frac{1}{\gamma}$ diffusion

in equilibrium $\rho = \rho_0 e^{-U/kT} \rightarrow \frac{\partial \rho}{\partial \underline{r}} = -\frac{1}{kT} \frac{\partial U}{\partial \underline{r}} \rho$

$= \frac{1}{kT} \underline{F} \rho$

$\underline{j} = 0$ in equilibrium $\rightarrow \mu = D/kT \rightarrow \gamma = kT/D$

— x —

Rotational Brownian motion:

random torques + rotational drag

$$\underline{\underline{I}} \cdot \frac{d\underline{\omega}}{dt} = \underline{N} - \tilde{\gamma} \underline{\omega} + \sqrt{2 \tilde{\gamma} kT} \, \tilde{\eta}(t)$$

explicit torque

rotational drag $\tilde{\gamma} = 8\pi\mu a^3$ for spheres

random torque $\underline{r} \times \underline{\eta}(t)$

Overdamped limit:

(i) $v(0) e^{-\gamma t/m}$ is the "inertial" term - persistence of motion decays on time scale $\frac{m}{\gamma} \sim 10^{-7}$ s (see below) explicitly:

$$\alpha \equiv \gamma/m$$

$$\langle (x(t)-x(0))\, v(t) \rangle$$

$$= \frac{1}{m^2} \int_0^t dt' \int_0^{t'} dt'' \, e^{-\alpha(t'-t'')} \int_0^t d\tau \, e^{-\alpha(t-\tau)} \langle \eta(t'')\eta(\tau) \rangle$$

$$\langle \eta(t'')\eta(\tau) \rangle = 2\gamma kT\, \delta(t''-\tau)$$

$$\int_0^{t'} dt'' \, \delta(t''-\tau) = \theta(t'-\tau)$$

$$= \frac{2\gamma kT}{m^2} \int_0^t d\tau \int_\tau^t dt' \, e^{-\alpha(t+t'-2\tau)}$$

$$= \frac{2\gamma kT}{m^2 \alpha} \int_0^t d\tau \left[e^{-\alpha(t-\tau)} - e^{-2\alpha(t-\tau)} \right]$$

$$= \frac{2\gamma kT}{m^2 \alpha^2} \left[\left(1-e^{-\alpha t}\right) - \frac{1}{2}\left(1-e^{-2\alpha t}\right) \right]$$

$$\xrightarrow[t\to\infty]{} \frac{\gamma kT}{m^2 \alpha^2} = \frac{kT}{\gamma}.$$

(2) Often $Re \simeq 0$ → force free motion → $m\ddot{\underline{r}} = 0$

(3) Scaling argument below

Then $\dot{\underline{r}}(t) = \frac{1}{\gamma}\left[\underline{F} + \sqrt{2\gamma kT}\, \eta \right]$ = Common approx.

— & —

Numerical methods

full Langevin eq. : use VV with F+η combined

or variant in A+T

overdamped eq. : simple version

$$\underline{r}(t+\Delta t) = \underline{r}(t) + \frac{1}{\gamma}\left[\underline{F}\,\Delta t + \sqrt{''}\, r_i \sqrt{\Delta t} \right]$$

normal random #

better : $\hat{\underline{r}}(t+\Delta t) = \underline{r}(t) + \frac{1}{2\gamma} F(\underline{r}(t))\,\Delta T$

$$\underline{r}(t+\Delta t) = \hat{r}(t) + \frac{1}{2\gamma} F(\hat{\underline{r}}(t)) + \frac{1}{\gamma} r_i \sqrt{\Delta T}$$

averages force over old + intermediate positions

NB: usual ODE convergence estimates not applicable

because random force differs

test by comparing $\langle \underline{v}(t) \rangle$ to known solution

Direct derivation of Langevin Eq ?

formal version from "Mori-Zwanzig" method

(Google it, or see Evans + Morriss, Stat Mech of Non Eq Liq.)

start from exact eq for $A(\{\underline{r}_i, \underline{p}_i\})$

$$\frac{dA}{dt} = \sum_i \frac{\partial A}{\partial \underline{r}_i} \cdot \dot{\underline{r}}_i + \frac{\partial A}{\partial \underline{p}_i} \cdot \dot{\underline{p}}_i = \sum_i \left(\frac{\partial H}{\partial \underline{p}_i} \cdot \frac{\partial}{\partial \underline{r}_i} - \frac{\partial H}{\partial \underline{r}_i} \frac{\partial}{\partial \underline{p}_i} \right) A$$

$\equiv \mathcal{L} A$ $\quad$ $\mathcal{L}$ = time-evolution operator (Liouville op.)

formal solution $A(t) = e^{\mathcal{L} t} A$ but not useful.

Idea: separate motion "along A" - slow variables

from rapid fluctuations in both variables

$$P_A \cdot X = \frac{(X, A)}{(A, A)} X \qquad (A, B) = \text{inner product}$$

rearrange time evolution using identity

$$e^{\mathcal{L}t} = e^{(1-P)\mathcal{L}t} + \int_0^t ds\, e^{\mathcal{L}(t-s)} P \mathcal{L} e^{(1-P)\mathcal{L}s}$$

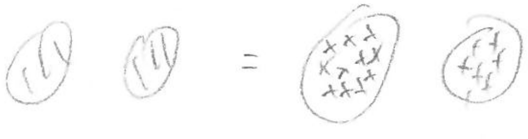
$$\rightarrow \dot{A}(t) = \Omega A(t) + \int ds\, K(s) A(t-s) + F(t)$$

formal expression $\qquad$ random

Then make some approx for Ω + K.

Specialize to suspensions (colloids in liquid)

Forces: gravity, E+M, and van der Waals



add vdW forces from atoms

→ vdW between bigger objects

e.g.

atom near solid has vdW force

$$\underline{F} = \int_{z<0} d^3r \, u_\varepsilon \left[\left(\frac{\sigma}{|\underline{r}_0 - \underline{r}|} \right)^{12} - \left(\frac{\sigma}{|\underline{r}_0 - \underline{r}|} \right)^{6} \right]$$

$$\sim \frac{\alpha}{z^9} - \frac{\beta}{z^3} \qquad \alpha, \beta = \text{calculable}$$

for a sphere near a wall, integrate ↑ over sphere atoms

$$-\frac{C}{r^6} \rightarrow -\frac{\pi^2 C \rho_1 \rho_2 R}{D} \quad \text{for } \sigma \ll D \ll R$$

This + electrostatics → DLVO interaction

2 spheres

same with $R \to \frac{R_1 R_2}{R_1 + R_2}$

Table in Israelachvili, Intermolecular + Surface Forces.

Macromolecules or irregular shapes?

use potential of mean force $V_{MF} = -kT \log g(r)$

Also flow-induced forces:

motion of #1 → flow at #2 → force on #2 etc.

$$\underset{\text{sphere}}{\gamma \dot{R}} \to \underset{\text{general shape}}{\underline{\underline{\gamma}} \cdot \dot{\underline{R}}} \to \sum_j \underline{\underline{\gamma}}_{ij} \cdot \dot{\underline{R}}_j + \sum \underline{\underline{\zeta}}_{ij} \cdot \underline{\omega}_j$$

$$\hat{\gamma}\,\omega \to \underline{\underline{\hat{\gamma}}} \cdot \underline{\omega} \to \sum_j \underline{\underline{\zeta}}^T_{ij} \cdot \dot{\underline{R}}_j + \sum \underline{\underline{\eta}}_{ij} \cdot \underline{\omega}_j$$

γ_{ij} = linear drag on i due to translation of j, etc.

$= f(r_{ij})$ + this requires special treatment.

Scaling analysis: $m\ddot{\underline{r}} + \gamma \dot{\underline{r}} = \underline{F} + \sqrt{2\gamma kT}\,\underline{\eta}(t)$

take sphere of radius a with diffusivity D

$\underline{r} = a\underline{R}$, $t = \frac{a^2}{D} T = \frac{a^2\gamma}{kT} T$ using SE

let $\underline{\eta}(t) = b\,\underline{H}(T)$ so

$$\langle \eta_i(t)\,\eta_j(t')\rangle = \begin{cases} b^2 \langle H_i(T)\,H_j(T')\rangle \\ \delta_{ij}\,\delta(t-t') = \delta_{ij} \left|\frac{dT}{dt}\right| \delta(T-T') \end{cases}$$

so $\langle H_i(T)\,H_j(T')\rangle = \delta_{ij}\,\delta(T-T')$ if $b = \sqrt{\frac{dT}{dt}} = \sqrt{\frac{kT}{a^2\gamma}}$

Then
$$\frac{ma}{(a^2\gamma/kT)^2} \frac{d^2R}{dT^2} + \underbrace{\gamma \frac{a}{a^2\gamma/kT}}_{kT/a} \frac{dR}{dT} = -\frac{1}{a}\frac{\partial U}{\partial R} + \underbrace{\sqrt{2\gamma kT}\sqrt{\frac{kT}{a^2\gamma}}}_{\sqrt{2}\,kT/a}\,\underline{H}(T)$$

or $\underbrace{\frac{mkT}{a^2\gamma^2}}_{\text{small ?}} \frac{d^2\underline{R}}{dT^2} + \frac{d\underline{R}}{dT} = -\frac{\partial}{\partial \underline{R}}\left(U/kT\right) + \sqrt{2}\,\underline{H}(T)$

take $a = 10^{-6}\,m$, $kT = 300^\circ \approx 10^{-21}\,J$, $\rho = 10^3\,kg/m^3$,

$m = \frac{4}{3}\pi a^3 \rho \cong 4 \times 10^{-15}\,kg$

$\gamma = 6\pi\mu a \cong 2 \times 10^{-8}\,kg/s$

so $\frac{m}{\gamma} = 2 \times 10^{-7}\,s$: small viscous time scale

$\frac{mkT}{\gamma^2 a^2} \sim 10^{-8}$: neglect $\ddot{\underline{R}}$ term ?

$\Rightarrow$ when γ = constant $\frac{d\underline{R}}{dT} = -\frac{\partial}{\partial \underline{R}}\left(U/kT\right) + \sqrt{2}\,H(T)$

or $\dot{\underline{r}} = \frac{1}{\gamma}\left[\left(-\frac{\partial U}{\partial r}\right) + \sqrt{2\gamma kT}\,\eta(t)\right]$

$\Rightarrow$ but when γ varies, keep the rhs :

$\underline{R}(T+\Delta T) - \underline{R}(T) = \int_T^{T+\Delta T} dT' \left[\underline{F}/kT + \sqrt{2}\,H(T') - \frac{mkT}{a^2\gamma^2(R)}\ddot{\underline{R}}\right]$

$= \frac{F}{kT}\Delta T + \sqrt{2\Delta T}\, r_i - \frac{mkT}{a^2}\int_T^{T+\Delta T} dT' \frac{1}{\gamma^2(R(T'))}\ddot{\underline{R}}(T')$

last term $= -\frac{mkT}{a^2}\left[\underbrace{\frac{1}{\gamma^2}\dot{R}(T')\Big|_T^{T+\Delta T}}_{\text{small}} - \int_T^{T+\Delta T} dT'\,\dot{\underline{R}}(T')\,\frac{-2}{\gamma^3}\left(\frac{\partial\gamma}{\partial \underline{R}}\cdot\dot{\underline{R}}\right)\right.$

last term here has $\dot{\underline{R}}\dot{\underline{R}} \xrightarrow[\text{equil}]{} \dfrac{\gamma^2 a^2}{mkT}\underline{\underline{1}}$

because $\left\langle \dfrac{d\underline{r}}{dt}\dfrac{d\underline{r}}{dt} \right\rangle = \dfrac{kT}{m}\underline{\underline{1}} = \dfrac{a^2}{(\gamma a^2/kT)^2}\left\langle \dfrac{d\underline{R}}{dT}\dfrac{d\underline{R}}{dT} \right\rangle$

so last term $\to -2\dfrac{1}{\gamma}\dfrac{d\gamma}{d\underline{R}}\,\Delta T = O(\Delta T)$!

Back to original variables:

vector of normal random #s

$$\dot{\underline{r}} = \frac{D}{kT}\left(\underline{F} + \right.$$

$$\to \underline{r}(t+\Delta t) = \underline{r}(t) + \frac{D}{kT}\underline{F} + \frac{D}{kT}\sqrt{2\gamma kT}\,\underline{n}\cdot\sqrt{\Delta t} - \frac{m}{kT}\int_t^{t+\Delta t} dt'\,D\ddot{\underline{r}}$$

$$\text{last term} = -\frac{m}{kT}\left[D\dot{\underline{r}}\Big|_t^{t+\Delta t} - \int_t^{t+\Delta t} dt\,\underbrace{\dot{\underline{r}}\left(\frac{\partial D}{\partial \underline{r}}\cdot\dot{\underline{r}}\right)}_{\to \frac{kT}{m}\frac{\partial D}{\partial \underline{r}}}\right.$$

or $$\underline{r}(t+\Delta t) = \underline{r}(t) + \left(\frac{D}{kT}\underline{F} + \nabla D\right)\Delta t + \sqrt{2D\Delta t}\,\underline{n}$$

Extra term due to Ermack + McConnell; JCP 69, 1352 (1978)

N-particle case: $\underline{R} = \begin{pmatrix} r_1 \\ \vdots \\ r_N \end{pmatrix}$ $\quad \underline{\underline{D}} = kT\underline{\underline{\gamma}}^{-1}$ $\quad \underline{\underline{\alpha}} \equiv$ "$\sqrt{\underline{\underline{D}}}$"

or $\underline{\underline{\alpha}}\underline{\underline{\alpha}}^T = \underline{\underline{D}}$

$$\underline{R}(t+\Delta t) = \underline{R}(t) + \left(\frac{1}{kT}\underline{\underline{D}}\cdot\underline{F} + \nabla\cdot\underline{\underline{D}}\right)\Delta t + \underline{\underline{\alpha}}\cdot\underline{n}\,\sqrt{\Delta t}$$

+ with rotation

$\underline{R} \to \begin{pmatrix} r_1 \\ r_N \\ \theta_1 \\ \theta_N \end{pmatrix}$ $\quad \underline{\underline{D}} \to kT\begin{pmatrix} \underline{\underline{\gamma}} & \underline{\underline{\xi}} \\ \underline{\underline{\xi}}^T & \underline{\underline{\eta}} \end{pmatrix}^{-1}$ $\Rightarrow$ Stokesian Dynamics

Fokker - Planck Eq.

$$\text{BD}: \quad \dot{\underline{x}}(t) = f(\underline{x}(t)) + \underline{\eta}(t), \quad \langle \eta_i \eta_j \rangle = \Delta \delta_{ij}\, \delta(t-t')$$

Problem is that this is a single trajectory = single realization of η & this does not itself capture the avg. behavior: a single random walk is just some scrawl. → need lots of averages

Would like a single eq. for the average.

One trajectory has the pdf $P_1(\underline{x},t) = \delta(\underline{x} - \underline{x}(t))$

↳ prob. of being at $\underline{x}$ at time t

so the average is $P(\underline{x}\,t) = \langle \delta(\underline{x} - \underline{x}(t)) \rangle$ ↖ avg over $\eta(t)$

Since $\underline{x}$ satisfies a 1st order ODE, P is uniquely determined from its initial condition: $P = P(\underline{x},t / \underline{x}_0, 0)$ $\quad \underline{x}_0 = \underline{x}(0)$

At any intermediate time, the particle is somewhere, so

$$P(\underline{x}, t+\varepsilon / x_0) = \int d\underline{y}\, P(\underline{x}, t+\varepsilon / \underline{y}, t)\, P(\underline{y}, t / x_0)$$

called the Chapman-Kolmogorov Eq.

Each realization of η has

$$\underline{x}(t+\varepsilon) = x(t) + \varepsilon f(\underline{x}(t)) + \int_t^{t+\varepsilon} dt'\, \eta(t')$$

$$\xrightarrow[\text{notation}]{\text{adjust}} \quad y(t) + \varepsilon f(y(t)) + \underline{H}^\varepsilon$$

So $P(\underline{x}, t+\varepsilon / \underline{y}, t) = \langle \delta(\underline{x} - y(t) - \varepsilon f(y(t)) - \underline{H}^\varepsilon) \rangle$

expand $\delta(\cdots) = \delta(\underline{x}-\underline{y}) + (\varepsilon \underline{f} + \underline{H}^{\varepsilon}) \cdot \frac{\partial}{\partial \underline{x}} \delta(\underline{x}-\underline{y}) +$

$$+ \frac{1}{2} \sum_{ij} (\varepsilon f_i + H_i^{\varepsilon})(\varepsilon f_j + H_j^{\varepsilon}) \frac{\partial^2}{\partial x_i \partial x_j} \delta(x-y) + \cdots$$

so $\langle \delta(\cdots) \rangle = \delta(\underline{x}-\underline{y}) - \varepsilon \underline{f}(y(t)) \cdot \frac{\partial}{\partial \underline{x}} \delta(\underline{x}-\underline{y}) +$

$$+ \frac{1}{2} \varepsilon \Delta \frac{\partial^2}{\partial \underline{x}^2} \delta(x-y) + O(\varepsilon^2)$$

because $\langle \underline{H}^{\varepsilon} \rangle = \int_t^{t+\varepsilon} dt' \langle \eta(t') \rangle = 0$

$$\langle H_i^{\varepsilon} H_j^{\varepsilon} \rangle = \int_0^{t+\varepsilon} dt' dt' \langle \eta_i(t) \eta_j(t') \rangle = \delta_{ij} \Delta \varepsilon$$

So $P(x, t+\varepsilon / x_0) = P(x, t / x_0) + \varepsilon \Big\{ - \int dy\, \underline{f}(y) P(yt/x_0) \cdot \frac{\partial}{\partial \underline{x}} \delta(x-y)$

$$+ \frac{1}{2} \Delta \int dy\, P(yt/x_0) \frac{\partial^2}{\partial \underline{x}^2} \delta(\underline{x}-\underline{y}) \Big\} + O(\varepsilon^2)$$

Use $\int dy\, \varphi(y) \frac{\partial}{\partial x} \delta(x-y) = \int dy\, \varphi(y) \left(-\frac{\partial}{\partial y} \delta(\underline{x}-\underline{y})\right)$

$$\xrightarrow{\text{ibp}} \int dy \frac{\partial \varphi(y)}{\partial y} \delta(\underline{x}-\underline{y}) = \frac{\partial \varphi(\underline{x})}{\partial \underline{x}}$$

$$\Rightarrow \boxed{\frac{\partial}{\partial t} P(\underline{x}, t / x_0) = -\frac{\partial}{\partial \underline{x}} (\underline{f} P) + \frac{1}{2} \Delta \frac{\partial^2 P}{\partial \underline{x}^2}} \quad \text{FP Eq.}$$

Special case: $\underline{f} = 0$, $\dot{\underline{x}} = \eta(t)$ $\rightarrow$ $\frac{\partial P}{\partial t} = \frac{1}{2} \Delta \frac{\partial^2 P}{\partial \underline{x}^2}$

random walk $\leftrightarrow$ diffusion eq.

Single particle: $\dot{\underline{x}} = \underline{p}/m$

$$\dot{\underline{p}} = \underline{F} - (\gamma/m) \underline{p} + \eta$$

or $\underline{x} = \begin{pmatrix} \underline{r} \\ \underline{p} \end{pmatrix}$ $\underline{f} = \begin{pmatrix} \underline{p}/m \\ \underline{F} - \gamma \underline{p}/m \end{pmatrix}$, $\underline{\eta} = \begin{pmatrix} 0 \\ \underline{\eta} \end{pmatrix}$

$$\frac{\partial}{\partial t} P(\underline{r}, \underline{p}) = -\frac{\partial}{\partial \underline{r}} \cdot \left(\underline{p}/m \, P \right) - \frac{\partial}{\partial \underline{p}} \cdot \left[\left(\underline{F} - \gamma \underline{p}/m \right) P \right] + \frac{\Delta}{2} \frac{\partial^2 P}{\partial \underline{p}^2}$$

Look for equilibrium solution $P_{eq} \propto \exp -\frac{1}{kT}\left(\underline{p}^2/2m + U(\underline{r}) \right)$

$$\frac{\partial P_{eq}}{\partial t} = \Big[-\underline{p}/m \cdot \left(-\frac{1}{kT} \frac{\partial U}{\partial \underline{r}} P \right) + \frac{\partial U}{\partial \underline{r}} \cdot \left(-\underline{p}/mkT \, P \right)$$

$$+ \frac{\gamma}{m} \frac{\partial}{\partial \underline{p}} \cdot \left(\underline{p} P \right) + \frac{\Delta}{2} \frac{\partial}{\partial \underline{p}} \cdot \left(-\underline{p}/mkT \, P \right) \Big]$$

$= 0$ if $\Delta = 2\gamma kT$.

$\therefore$ FDT with interactions

Solving FP eq: $\begin{cases} \text{linear hyperbolic PDE} \\ \text{messy } \underline{r}\text{-dependent coefficients} \end{cases}$

lots of analytic + numerical methods
See H. Risken, "The Fokker-Planck Eq."

General case: $\dot{\underline{x}} = \underline{f}(\underline{x},t) + \underline{\underline{A}}(\underline{x},t)\cdot\underline{\eta}(t)$

$$\rightarrow \quad \frac{\partial P(\underline{x},t)}{\partial t} = -\frac{\partial}{\partial \underline{x}}\cdot(\underline{f}P) + \frac{\partial}{\partial \underline{x}}\cdot\left[\underline{\underline{A}}\cdot\left(\frac{\partial}{\partial \underline{x}}\cdot\underline{\underline{A}}^T P\right)\right]$$

using same method as for $A = 1$

Apply to
$$\begin{cases} \dot{\underline{p}}_i = -\sum_j \underline{\underline{\gamma}}_{ij}\,\underline{p}_j/m_j + \underline{F}_i + \sum_j \underline{\underline{\alpha}}_{ij}\cdot\underline{\eta}_j \\ \dot{\underline{r}}_i = 0 \end{cases}$$

Here $\underline{F}_i = \frac{\partial V}{\partial \underline{r}_i}$ $\quad \langle \eta_i(t)\eta_j(t')\rangle = \delta_{ij}\,\delta(t-t')$

$$\underline{x} = \begin{pmatrix} \underline{r}_i \\ \underline{p}_i \end{pmatrix} \quad \underline{f} = \begin{pmatrix} \underline{p}_i/m_i \\ \underline{F}_i - \gamma\underline{p}_i/m_i \end{pmatrix} \quad \underline{\underline{A}} = \begin{pmatrix} \underline{\underline{0}} & \underline{\underline{0}} \\ \underline{\underline{0}} & \underline{\underline{\alpha}} \end{pmatrix}$$

$$\text{so} \quad \frac{\partial P}{\partial t} = -\sum_i \frac{\partial}{\partial \underline{r}_i}\cdot\left(\frac{\underline{p}_i}{m_i}P\right) - \frac{\partial}{\partial \underline{p}_i}\cdot\left[\left(\underline{F}_i - \underline{\underline{\gamma}}_{ij}\,\underline{p}_j/m_j\right)P\right]$$
$$+ \frac{\partial}{\partial \underline{p}_i}\cdot\left[\underline{\underline{\alpha}}\cdot\frac{\partial}{\partial \underline{p}_i}\cdot\left(\underline{\underline{\alpha}}\,P\right)\right]$$

set $\quad P \propto \exp -\frac{1}{kT}\left(\sum_i p_i^2/m_i + V(\{r_i\})\right)$

then $\quad \frac{\partial P}{\partial t} = 0 \ldots$ if $\quad \underline{\underline{\alpha}}_i\,\underline{\underline{\alpha}}_i^T = \underline{\underline{\gamma}}\,kT$