AN INTRODUCTION TO BROWNIAN MOTION AND BROWNIAN DYNAMICS

OBJECTIVE: Efficient treatment of problems in which motion is characterized by wide time scale separation.
[Large number of fast moving degrees of freedom, the details of whose motion are relatively uninteresting, coexist with a smaller number of slower degrees of freedom, on whose motion we wish to focus].

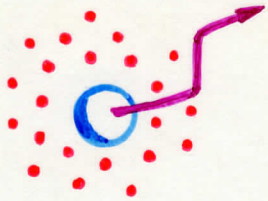
Basic idea: Treat the fast motion in a collective sense.
(fast degrees of freedom represented by a combination of random forces and frictional terms arising due to interaction of slower degrees of freedom, or "Brownian particles", with a heat bath.)

HISTORY: Robert Brown (1827). Erratic motion in suspensions of fine particles, not of organic origin.

A. Einstein (1905): "Über die von der molekular-kinetischen Theorie der Wärme geforderte Bewegung von in ruhenden Flüssigkeiten suspendierten Teilchen".

Smoluchowski, Fokker, Planck, Kramers, Chandrasekhar, Zwanzig, Mo

1. The Brownian Motion Model.



Brownian particle, mass m.

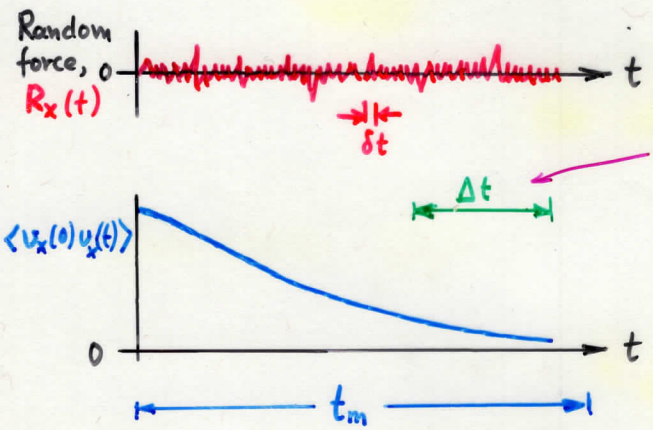
Bath of solvent molecules, temperature T.

Slow change of position and velocity of the Brownian particle:
characteristic time t_m.

Fast, frequent collisions between Brownian particle and bath particles:
characteristic time δt.

$t_m \gg \delta t$: Two widely disparate timescales.

Particle / Bath interaction:
- Randomly fluctuating force, $\underset{\sim}{R}(t)$ (collisions)
- Frictional force, $\propto \underset{\sim}{v}(t)$ ← Particle velocity.



∃ intermediate time scale Δt
such that $\delta t \ll \Delta t \ll t_m$

The Langevin Equation (1908)

A stochastic equation of motion for a Brownian particle

$$m\,\dot{\underset{\sim}{v}}(t) = -\xi\, m\, \underset{\sim}{v}(t) + \underset{\sim}{R}(t) \qquad (1.1)$$

ξ: friction coefficient (dimensions: time^{-1}) — FRICTIONAL FORCE

$\underset{\sim}{R}(t)$: RANDOM (LANGEVIN) FORCE

This is a stochastic differential equation.
It does not describe a definite trajectory. Its solution, subject to given initial conditions, is a random function of time.

Properties of the Random Force

$$\langle \underset{\sim}{R}(t) \rangle = 0 \qquad \text{(NO DIRECTIONAL PREFERENCE)} \qquad (1.2)$$

($\langle\ \rangle$: ensemble average)

$$\langle \underset{\sim}{R}(t) \cdot \underset{\sim}{v}(0) \rangle = 0 \qquad \text{(NO CORRELATION WITH VELOCITY)} \qquad (1.3)$$

Autocorrelation function:

$$\langle \underset{\sim}{R}(t+s) \cdot \underset{\sim}{R}(s) \rangle = R_0\, \delta(t) \qquad (1.4)$$

($\delta(t)$: Dirac delta function; R_0: a constant (units of force^2 × time))

Physical interpretation: $\underset{\sim}{R}(t)$ has an infinitesimally short memory!
(immediately becomes uncorrelated with itself)
"Underlying Markovian Hypothesis"

NOTE: The power spectrum of the random force, i.e. the Fourier transform of its time autocorrelation function, is a constant:

$$\int_{-\infty}^{+\infty} \langle \underset{\sim}{R}(t) \cdot \underset{\sim}{R}(0) \rangle \exp(i\omega t)\, dt = R_0 \int_{-\infty}^{+\infty} \delta(t) \exp(i\omega t)\, dt = R_0$$

"WHITE NOISE"

Some simple consequences of the Langevin equation.

Formal solution, subject to the condition $\underset{\sim}{v} = \underset{\sim}{v}(0)$ at $t=0$:
[compare solution of 1st order ODEs]:

$$m\,\underset{\sim}{v}(t) = m\,\underset{\sim}{v}(0) \exp(-\xi t) + \exp(-\xi t) \int_0^t \exp(\xi s)\, \underset{\sim}{R}(s)\, ds \qquad (1.5)$$

- There is a connection between frictional and random forces (ξ and R_0).

Square eq (1.5) and ensemble average:

$$m^2 \langle |\underset{\sim}{v}(t)|^2 \rangle = m^2 \langle |\underset{\sim}{v}(0)|^2 \rangle \exp(-2\xi t) + m \exp(-2\xi t) \int_0^t \exp(\xi s) \langle \underset{\sim}{R}(s) \cdot \underset{\sim}{v}(0) \rangle ds$$

$\langle \underset{\sim}{R}(s) \cdot \underset{\sim}{v}(0) \rangle = 0$ (1.3)

$$+ \exp(-2\xi t) \int_0^t ds \int_0^t ds' \exp[\xi(s+s')] \underbrace{\langle \underset{\sim}{R}(s) \cdot \underset{\sim}{R}(s') \rangle}_{R_0\,\delta(s-s')} =$$

$$= m^2 \langle |\underset{\sim}{v}(0)|^2 \rangle \exp(-2\xi t) + \frac{R_0}{2\xi} [1 - \exp(-2\xi t)] \qquad (1.6)$$

In the limit $t \to \infty$, the particle will become thermally equilibrated with the bath:

$$\langle |\underset{\sim}{v}(\infty)|^2 \rangle \equiv \frac{3 k_B T}{m} \overset{(1.6)}{=} \frac{R_0}{2\xi m^2}$$

equil. ensemble average kinetic energy $\frac{1}{2} k_B T$ per degree of freedom

Hence, $$\xi = \frac{R_0}{6 m k_B T} = \frac{\beta}{6m} R_0 = \frac{\beta}{3m} \int_0^\infty \langle \underset{\sim}{R}(t) \cdot \underset{\sim}{R}(0) \rangle \, dt \qquad (1.7)$$

a "FLUCTUATION-DISSIPATION" theorem

Eq. (1.7) relates the magnitude of fluctuations in the random force to the friction coefficient. Both the frictional and the Langevin force have the same physical origin, i.e. interactions with the fast degrees of freedom. Eq. (1.7) can also be found in the form

$$\langle \underset{\sim}{R}(t) \cdot \underset{\sim}{R}(0) \rangle = 6 \frac{m\xi}{\beta} \delta(t) = 2\xi \langle \underset{\sim}{p}^2 \rangle \delta(t)$$

equil. ensemble average of particle sq. momentum.

- There is a relation between ξ and the self-diffusivity, D.

Langevin equation (1.1) can be converted into a differential equation in the ensemble averaged mean squared displacement:

$$(1.1) \Rightarrow m \underset{\sim}{r} \cdot \dot{\underset{\sim}{v}} + \xi m \underset{\sim}{r} \cdot \underset{\sim}{v} = \underset{\sim}{r} \cdot \underset{\sim}{R} \Rightarrow$$

$$\Rightarrow m \left(\frac{1}{2} \frac{d^2}{dt^2} \underset{\sim}{r}^2 - \underset{\sim}{v}^2 \right) + \xi m \left(\frac{1}{2} \frac{d}{dt} \underset{\sim}{r}^2 \right) = \underset{\sim}{r} \cdot \underset{\sim}{R}$$

Ensemble average:

$$\frac{m}{2}\frac{d^2}{dt^2}\langle|\underset{\sim}{r}(t)|^2\rangle + \xi\frac{m}{2}\frac{d}{dt}\langle|\underset{\sim}{r}(t)|^2\rangle = \underbrace{m\langle|\underset{\sim}{v}(t)|^2\rangle}_{3k_BT,\ \text{assume equilibrium!}} + \langle \underset{\sim}{r}(t)\cdot\underset{\sim}{R}(t)\rangle$$

(the last term $\to 0$)

or

$$\frac{d^2}{dt^2}\langle|\underset{\sim}{r}(t)|^2\rangle + \xi\frac{d}{dt}\langle|\underset{\sim}{r}(t)|^2\rangle = \frac{6k_BT}{m} \qquad (1.8)$$

with initial conditions $\langle|\underset{\sim}{r}(0)|^2\rangle = 0$, $\frac{d}{dt}\langle|\underset{\sim}{r}(t)|^2\rangle_{t=0} = 2\langle\underset{\sim}{r}(0)\cdot\underset{\sim}{v}(0)\rangle =$

Solution: $$\langle|\underset{\sim}{r}(t)|^2\rangle = \left(\frac{6k_BT}{\xi m}\right)\left(t - \frac{1}{\xi} + \frac{1}{\xi}\exp(-\xi t)\right) \qquad (1.9)$$

Short times $(\xi t << 1)$: $\langle|\underset{\sim}{r}(t)|^2\rangle = \frac{3k_BT}{m}t^2 = \langle v^2\rangle t^2$

(free particle motion)

Long times $(\xi t >> 1)$: $\langle|\underset{\sim}{r}(t)|^2\rangle = \frac{6k_BT}{\xi m}t = 6Dt$

(diffusive motion)

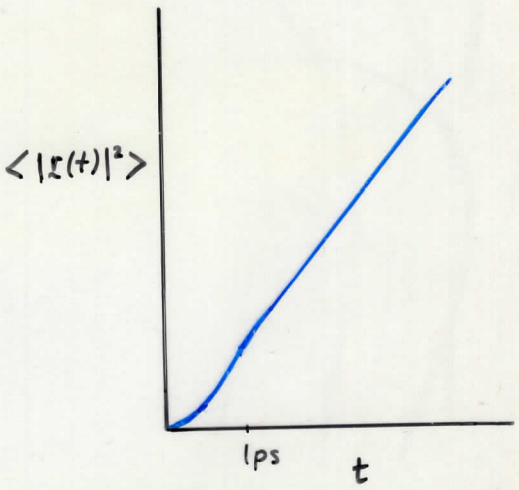
where $\boxed{D = \frac{k_BT}{\xi m}}$ (Einstein relation)

Estimate of ξ from continuum hydrodynamic analysis

Brownian particle diameter

$\xi = \frac{3\pi\eta d}{m}$ (Stokes) "stick"

$\xi = \frac{2\pi\eta d}{m}$ "slip"



Typical MD simulation result

Good correlation of experimental data on D, η, even for simple liquids!

- **The velocity autocorrelation function of a Brownian particle decays exponentially.**

For a Brownian particle *in equilibrium* with the heat bath, eq (1.5) gives:

$$C_{\underline{v}\underline{v}}(t) = \langle \underline{v}(0)\cdot\underline{v}(t)\rangle = \underbrace{\langle|\underline{v}(0)|^2\rangle}_{\text{equilibrium}} \exp(-\xi t) + \exp(-\xi t)\int_0^t e^{\xi s}\langle \underline{R}(s)\cdot\underline{v}(0)\rangle \, ds$$

$\langle \underline{R}(s)\cdot\underline{v}(0)\rangle \to 0$

or

$$C_{\underline{v}\underline{v}}(t) = \frac{3k_BT}{m}\exp(-\xi t) \qquad (1.10)$$

$\xi^{-1} = \frac{mD}{k_BT}$ is a correlation time.

Exponential decay of time correlation functions is characteristic of Markov processes.

NOTE: $C_{\underline{v}\underline{v}}$ in a liquid does *not* decay exponentially.
(Short times: a molecule experiences few collisions with its neighbors, basic assumptions of Langevin theory do not hold. Long times: cooperative motion of molecules leads to "long time tails", $C_{\underline{v}\underline{v}} \sim t^{-3/2}$)

2. The Fokker-Planck and the Chandrasekhar equation.

The Langevin equation provides a stochastic description of the motion of a Brownian particle.
An equivalent description can be provided in terms of *differential equations* governing the *probability density* of the particle in phase space, momentum space, or configuration space.

Consider the case of a free (i.e. not subject to external fields) Brownian particle. Let $W(\underset{\sim}{v}, t)$ be the density function characterizing an ensemble of such particles in momentum space.
In other words, under given initial conditions, $W(\underset{\sim}{v}, t)\, d\underset{\sim}{v}$ is the probability of finding a particle with velocity vector $\underset{\sim}{v}$ to $\underset{\sim}{v} + d\underset{\sim}{v}$ at time t.

Let Δt be a time interval long enough for the random force $\underset{\sim}{R}(t)$ to undergo many fluctuations but short enough, so $\underset{\sim}{v}(t)$ does not change appreciably. Let

$\Psi(\underset{\sim}{v}, \Delta\underset{\sim}{v})$ = the probability that $\underset{\sim}{v}$ undergoes a change $\Delta\underset{\sim}{v}$ in the interval Δt.

For a Markov process, the course of the system at time t depends only upon the instantaneous state of the system at time t, and not upon its previous history. Such a stochastic process conforms to a fundamental equation of the form

$$W(\underset{\sim}{v}, t+\Delta t) = \int W(\underset{\sim}{v} - \Delta\underset{\sim}{v}, t)\, \Psi(\underset{\sim}{v} - \Delta\underset{\sim}{v}; \Delta\underset{\sim}{v})\, d(\Delta\underset{\sim}{v}) \qquad (2.1)$$

{ compare $\Pi_n^{(t+1)} = \sum_m \Pi_m^{(t)} P_{nm}$ in discrete Markov chains }

Eq (2.1) is known as the Chapman-Kolmogorov equation.

Now, expand $W(\underset{\sim}{v}, t+\Delta t)$, $W(\underset{\sim}{v} - \Delta\underset{\sim}{v}, t)$ and $\Psi(\underset{\sim}{v} - \Delta\underset{\sim}{v}, \Delta\underset{\sim}{v})$ in Taylor series:

$$(2.1) \Rightarrow W(\underset{\sim}{v}, t) + \frac{\partial W}{\partial t}\Delta t + O(\Delta t^2) =$$

$$\iiint_{-\infty}^{+\infty} d(\Delta u_1) d(\Delta u_2) d(\Delta u_3) \left[W(\underset{\sim}{v}, t) - \sum_\alpha \frac{\partial W}{\partial v_\alpha}\Delta v_\alpha + \frac{1}{2}\sum_\alpha \frac{\partial^2 W}{\partial v_\alpha^2}\Delta v_\alpha^2 + \sum_{\alpha<\beta} \frac{\partial^2 W}{\partial v_\alpha \partial v_\beta}\Delta v_\alpha \Delta v_\beta + \right.$$

$$\left. \times \left[\Psi(\underset{\sim}{v}; \Delta\underset{\sim}{v}) - \sum_\alpha \frac{\partial \Psi}{\partial v_\alpha}\Delta v_\alpha + \frac{1}{2}\sum_i \frac{\partial^2 \Psi}{\partial v_\alpha^2}\Delta v_\alpha^2 + \sum_{\alpha<\beta} \frac{\partial^2 \Psi}{\partial v_\alpha \partial v_\beta}\Delta v_\alpha \Delta \right. \right.$$

$(\alpha = 1, 2, 3)$

Now, introduce the abbreviations:

$$\langle \Delta v_\alpha \rangle = \int_{-\infty}^{+\infty} \Delta v_\alpha \; \psi(\underset{\sim}{v}; \Delta \underset{\sim}{v}) \, d(\Delta \underset{\sim}{v})$$

$$\langle \Delta v_\alpha^2 \rangle = \int_{-\infty}^{+\infty} \Delta v_\alpha^2 \; \psi(\underset{\sim}{v}; \Delta \underset{\sim}{v}) \, d(\Delta \underset{\sim}{v}) \qquad (2.2)$$

$$\langle \Delta v_\alpha \Delta v_\beta \rangle = \int_{-\infty}^{+\infty} \Delta v_\alpha \Delta v_\beta \; \psi(\underset{\sim}{v}; \Delta \underset{\sim}{v}) \, d(\Delta \underset{\sim}{v}).$$

Then,

$$\frac{\partial W}{\partial t} \Delta t + \mathcal{O}(\Delta t^2) = - \sum_\alpha \frac{\partial W}{\partial v_\alpha} \langle \Delta v_\alpha \rangle + \frac{1}{2} \sum_\alpha \frac{\partial^2 W}{\partial v_\alpha^2} \langle \Delta v_\alpha^2 \rangle +$$

$$+ \sum_{\alpha<\beta} \frac{\partial^2 W}{\partial v_\alpha \partial v_\beta} \langle \Delta v_\alpha \Delta v_\beta \rangle - \sum_\alpha W \frac{\partial \langle \Delta v_\alpha \rangle}{\partial v_\alpha} + \sum_\alpha \frac{\partial}{\partial v_\alpha} \langle \Delta v_\alpha^2 \rangle \frac{\partial W}{\partial v_\alpha} +$$

$$+ \sum_{\alpha<\beta} \frac{\partial W}{\partial v_\alpha} \frac{\partial \langle \Delta v_\alpha \Delta v_\beta \rangle}{\partial v_\beta} + \frac{1}{2} \sum_\alpha \frac{\partial^2}{\partial v_\alpha^2} \langle \Delta v_\alpha^2 \rangle W +$$

$$+ \sum_{\alpha<\beta} W \frac{\partial^2 \langle \Delta v_\alpha \Delta v_\beta \rangle}{\partial v_\alpha \partial v_\beta} + \cdots$$

which can be written more simply as

$$\frac{\partial W}{\partial t} \Delta t + \mathcal{O}(\Delta t^2) = - \sum_\alpha \frac{\partial}{\partial v_\alpha} \left(W \langle \Delta v_\alpha \rangle \right) + \frac{1}{2} \sum_\alpha \frac{\partial^2}{\partial v_\alpha^2} \left(W \langle \Delta v_\alpha^2 \rangle \right)$$

$$+ \sum_{\alpha<\beta} \frac{\partial^2}{\partial v_\alpha \partial v_\beta} \left(W \langle \Delta v_\alpha \Delta v_\beta \rangle \right) + \cdots \qquad (2.3)$$

Now, for a Brownian particle following the Langevin equation, the evolution of the velocity vector is given by (1.5). Using this equation between times t and $t+\Delta t$, we have:

$$\langle \Delta \underset{\sim}{v} \rangle \equiv \langle \underset{\sim}{v}(t+\Delta t) - \underset{\sim}{v}(t) \rangle = \langle \underset{\sim}{v}(t) \left[\exp(-\zeta \Delta t) - 1 \right] + \exp(-\zeta t) \int_0^t \exp(\zeta s) \, \underset{\sim}{R}(s) \, ds \rangle$$

(average in the sense of (2.2))

$$= \underset{\sim}{v}(t) \left[\exp(-\zeta \Delta t) - 1 \right] + \exp(-\zeta t) \int_0^t \exp(\zeta s) \langle \underset{\sim}{R}(s) \rangle \, ds$$

($\langle \underset{\sim}{R}(s) \rangle = 0$)

or $$\langle \Delta v_\alpha \rangle = v_\alpha \left[e^{-\xi \Delta t} - 1 \right] = -\xi v_\alpha \Delta t + \mathcal{O}(\Delta t^2) \qquad (2.4)$$

Similarly, using the precursor of eq (1.10) between times t and $t+\Delta t$,

$$\langle \Delta \underset{\sim}{v}^2 \rangle = \langle \left[\underset{\sim}{v}(t+\Delta t) - \underset{\sim}{v}(t) \right]^2 \rangle = \langle |\underset{\sim}{v}(t+\Delta t)|^2 \rangle + \langle |\underset{\sim}{v}(t)|^2 \rangle - 2 \langle \underset{\sim}{v}(t+\Delta t) \cdot \underset{\sim}{v}(t) \rangle =$$

$$= 2 \langle |\underset{\sim}{v}(t)|^2 \rangle - 2 \langle |\underset{\sim}{v}(t)|^2 \rangle \exp(-\xi \Delta t) + \mathcal{O}(\Delta t^2) =$$

$$= 2 \cdot \frac{3 k_B T}{m} \left[1 - \exp(-\xi \Delta t) \right] + \mathcal{O}(\Delta t^2) = 2 \cdot \frac{3 k_B T}{m} \cdot \xi \Delta t + \mathcal{O}(\Delta t^2)$$

hence $$\langle \Delta v_\alpha^2 \rangle = \frac{1}{3} \langle \Delta \underset{\sim}{v}^2 \rangle = \frac{2 \xi k_B T}{m} \Delta t + \mathcal{O}(\Delta t^2) \qquad (2.5)$$

Also, assuming that the components of $\underset{\sim}{R}(t)$ are uncorrelated, one obtains

$$\langle \Delta v_\alpha \Delta v_\beta \rangle = 0 \qquad \alpha \neq \beta. \qquad (2.6)$$

Using equations (2.3), (2.4), (2.5), (2.6), one obtains:

$$\frac{\partial W}{\partial t} \Delta t + \mathcal{O}(\Delta t^2) = \left\{ \xi \sum_\alpha \frac{\partial}{\partial v_\alpha} (W v_\alpha) + \xi \frac{k_B T}{m} \sum_\alpha \frac{\partial^2}{\partial v_\alpha^2} W \right] \Delta t + \mathcal{O}(\Delta t^2)$$

which, in the limit $\Delta t \to 0$, becomes:

$$\boxed{\frac{\partial W}{\partial t} = \xi \, \nabla_{\underset{\sim}{v}} \cdot (W \underset{\sim}{v}) + \frac{\xi k_B T}{m} \nabla_{\underset{\sim}{v}}^2 W} \qquad (2.7)$$

Fokker-Planck equation, governing the evolution of the probability density in momentum space.

Essentially, a diffusion equation for W in velocity space.

Stationary solution: Maxwell-Boltzmann.

Assuming that the evolution in phase space is Markovian, generalization of this argument for a particle experiencing an external (systematic) force field $\underset{\sim}{F} = -\nabla_{\underset{\sim}{r}} V$ (see McQuarrie, Chapter 20) leads to an equation for the probability density in phase space, $p(\underset{\sim}{r}, \underset{\sim}{v}, t)$.

$$\frac{\partial}{\partial t} p(\underset{\sim}{r}, \underset{\sim}{v}, t) + \underset{\sim}{v} \cdot \nabla_{\underset{\sim}{r}} p(\underset{\sim}{r}, \underset{\sim}{v}, t) + \frac{\underset{\sim}{F}}{m} \cdot \nabla_{\underset{\sim}{v}} p(\underset{\sim}{r}, \underset{\sim}{v}, t) = \xi \nabla_{\underset{\sim}{v}} \cdot [p(\underset{\sim}{r}, \underset{\sim}{v}, t) \underset{\sim}{v}] + \frac{\xi k_B T}{m} \nabla_{\underset{\sim}{v}}^2 p(\underset{\sim}{r}, \underset{\sim}{v}, t) \tag{2.8}$$

Chandrasekhar equation, governing the evolution of the probability density in phase space.
(The terms "Kolmogorov's equation", "Smoluchowski equation" are used loosely as synonyms of "Fokker-Planck" and "Chandrasekhar").

For times $\Delta t >> \xi^{-1}$ the evolution of a particle in configuration space can be viewed as a Markov process. Under these conditions, the Chapman-Kolmogorov equation in configuration space leads to an equation for the probability density $p(\underset{\sim}{r}, t)$:

function of position.

$$\frac{\partial}{\partial t} p(\underset{\sim}{r}, t) + \frac{D}{k_B T} \nabla_{\underset{\sim}{r}} \cdot \left(\underset{\sim}{F} p(\underset{\sim}{r}, t) \right) = D \nabla_{\underset{\sim}{r}}^2 p(\underset{\sim}{r}, t) \tag{2.9}$$

$$D = \frac{k_B T}{\xi m}$$

Smoluchowski equation, a common diffusion equation in configuration space.
(stationary solution: $p(\underset{\sim}{r}, t) \propto \exp\left(-\frac{V(\underset{\sim}{r})}{k_B T}\right)$

3. Microscopic Basis for the Brownian Motion Model: The Projection Operator formalism. (Zwanzig, Mori)

Reference: Deutsch, J.M.; Oppenheim, I. Faraday Discuss. Chem. Soc. 1987, 83, 1-20; Allen and Tildesley, Chap. 9.

OBJECTIVE:

- Derive a formalism similar to the Brownian motion model from the exact evolution equations describing the dynamics of a molecular system.
- Identify conditions, under which Brownian motion model is a reasonable representation of reality.

APPROACH:

Consider a system of N particles (e.g. solvent molecules and Brownian particle), described in phase space by $\underset{\sim}{r}^N$, $\underset{\sim}{p}^N$.

Let $\underset{\sim}{\mathcal{A}} = (\mathcal{A}_1, \ldots, \mathcal{A}_n)$ a set of dynamical variables, depending on $\underset{\sim}{r}^N$, $\underset{\sim}{p}^N$.

The evolution of $\underset{\sim}{\mathcal{A}}$ is described exactly by the Liouville equation.

$$\underset{\sim}{\mathcal{A}}\left(\underset{\sim}{r}^N(t), \underset{\sim}{p}^N(t)\right) = i\hat{\mathcal{L}}\,\underset{\sim}{\mathcal{A}}\left(\underset{\sim}{r}^N(t), \underset{\sim}{p}^N(t)\right) \qquad (3.1)$$

where $i\hat{\mathcal{L}} = \sum_i \dot{\underset{\sim}{r}}_i \nabla_{\underset{\sim}{r}_i} + \sum_i \dot{\underset{\sim}{p}}_i \cdot \nabla_{\underset{\sim}{p}_i} = \dot{\underset{\sim}{r}} \cdot \nabla_{\underset{\sim}{r}} + \dot{\underset{\sim}{p}} \cdot \nabla_{\underset{\sim}{p}}$ Liouville operator.

Formal solution to (3.1): $\underset{\sim}{\mathcal{A}}\left(\underset{\sim}{r}^N(t), \underset{\sim}{p}^N(t)\right) = \exp(i\hat{\mathcal{L}}t)\,\underset{\sim}{\mathcal{A}}\left(\underset{\sim}{r}^N(0), \underset{\sim}{p}^N(0)\right)$

This formulation is
- time reversible
- cumbersome to use (involves all degrees of freedom).

DEF. $\mathcal{A}_i, \mathcal{B}_i$ orthogonal, if $\langle \mathcal{A}_i \mathcal{B}_i \rangle = 0$ (← ens. average)

The projection operator formalism allows arriving from the Liouville equation to an equation of motion involving $\underset{\sim}{\mathcal{A}}$ and no other dynamical variables. This is done by projecting any dynamical variable onto $\underset{\sim}{\mathcal{A}}$, i.e. removing those parts that are orthogonal to $\underset{\sim}{\mathcal{A}}$.

Resulting exact equation of motion:

$$\dot{\underset{\sim}{\mathcal{A}}}(t) = i\underline{\underline{\Omega}}\,\underset{\sim}{\mathcal{A}}(t) - \int_0^t \underline{\underline{M}}(t')\,\underset{\sim}{\mathcal{A}}(t-t')\,dt' + \mathring{\underset{\sim}{\mathcal{A}}}(t) \qquad (3.2)$$

($\underset{\sim}{\mathcal{A}}(t) \leftarrow \underset{\sim}{\mathcal{A}}(\underset{\sim}{p}^N(t), \underset{\sim}{r}^N(t))$)

where $\underline{\underline{\Omega}}$ = frequency matrix; $i\underline{\underline{\Omega}} \equiv \langle \dot{\underset{\sim}{\mathcal{A}}}\,\underset{\sim}{\mathcal{A}} \rangle \langle \underset{\sim}{\mathcal{A}}\,\underset{\sim}{\mathcal{A}} \rangle^{-1}$ (← inverse; dyadics)

$i\underline{\underline{\Omega}}$: dimensions time^{-1}

$\mathring{\underset{\sim}{\mathcal{A}}}(t)$ = "random force". = the part of $\dot{\underset{\sim}{\mathcal{A}}}$ that is initially orthogonal to $\underset{\sim}{\mathcal{A}}(0)$ and evolves so as to remain orthogonal to $\underset{\sim}{\mathcal{A}}(0)$ at all subsequent times:

$$\langle \mathring{\underset{\sim}{\mathcal{A}}}(t)\,\underset{\sim}{\mathcal{A}}(0) \rangle = 0$$

$\underline{\underline{M}}(t)$ = "memory function matrix".

$$\underline{\underline{M}}(t) = \langle \mathring{\underset{\sim}{\mathcal{A}}}(t)\,\mathring{\underset{\sim}{\mathcal{A}}}(t) \rangle \langle \underset{\sim}{\mathcal{A}}\,\underset{\sim}{\mathcal{A}} \rangle^{-1}$$

The memory matrix is related to the autocorrelation matrix $\underline{\underline{C}}(t) = \langle \underset{\sim}{\mathcal{A}}(t)\,\underset{\sim}{\mathcal{A}}(0) \rangle$ by $\dot{\underline{\underline{C}}}(t) = i\underline{\underline{\Omega}}\,\underline{\underline{C}}(t) - \int_0^t \underline{\underline{M}}(t')\,\underline{\underline{C}}(t-t')\,dt'$.

The utility of this approach lies in that $\underline{\underline{M}}(t)$ may decay much more rapidly than $\underline{\underline{C}}(t)$. Thus, a simple stochastic model for $\mathring{\underset{\sim}{\mathcal{A}}}(t)$ (e.g., white noise) may give a satisfactory description of the system dynamics.

mass Brownian particle / volume Brownian partic

An example: Particle of mass m, density ρ, diameter d in a bath of particles of mass m_b, density ρ_b, at temp. T.

↳ total mass particles of bath / total volume of bath.

Select $\underset{\sim}{\alpha} \to \underset{\sim}{p}$ (momentum of large particle)

Then, $\underset{\sim}{\alpha}^{\circ} \to \underset{\sim}{p}^{\circ}$ (a random force!)

For $\varepsilon = \left(\frac{m_b}{m}\right)^{1/2} \ll 1$, $\frac{\rho_b}{\rho} \lesssim 1$, the projected equation of motion

reduces to $$\dot{\underset{\sim}{p}}(t) = \dot{\underset{\sim}{p}}^{\circ}(t) - \int_0^t \underset{\sim}{p}(t-\tau) \left(\frac{\beta}{3m} \langle \underset{\sim}{F} \cdot \underset{\sim}{F}_0(\tau) \rangle_0\right) d\tau$$

MEMORY FUNCTION $\underline{\underline{M}}(\tau)$

where $\underset{\sim}{F}$ = force on large particle due to both particles

subscript 0 : denotes a system of small particles at fixed position of the large particle

$\underset{\sim}{F}_0(\tau)$ indicates the force that would be exerted on the large particle at time τ, if the force on the large particle at time 0 were $\underset{\sim}{F}$ and the large particle remained stationary since time 0, so that the whole system evolved according to the Hamiltonian of the small particles.

If, in addition, $\frac{\rho_b}{\rho} \ll 1$ the equation reduces further to

$$\dot{\underset{\sim}{p}}(t) = \dot{\underset{\sim}{p}}^{\circ}(t) - \left\{\frac{\beta}{3m} \int_0^{\infty} \langle \underset{\sim}{F} \cdot \underset{\sim}{F}_0(\tau) \rangle_0 \, d\tau\right\} \underset{\sim}{p}(t)$$

Langevin force

Friction coefficient ξ

Furthermore, if $\frac{d a^2}{\ell^3} \ll 1$, with a = range of intermolecular force, ℓ = distance between bath particles

then $\xi = \frac{2\pi\eta d}{m}$ (Stokes)

4. Brownian Dynamics Simulation: Numerical Solution of the Langevin Equation.

4.1. Integration of the Langevin equation in Configuration and Momentum Space

The problem: Integrate $m\dot{\underset{\sim}{v}}(t) = -m\xi\,\underset{\sim}{v}(t) + \underset{\sim}{F}(\underset{\sim}{r}) + \underset{\sim}{R}(t)$ (4.1)
subject to given $\underset{\sim}{r}(0)$, $\underset{\sim}{v}(0)$. ← ext. field.

- Equation (4.1) is stochastic. Only representative trajectories can be generated.

- The random force $\underset{\sim}{R}(t)$ is invariably assumed to be a Gaussian white noise, with

$$\langle \underset{\sim}{R}(t) \rangle = \underset{\sim}{0} \qquad (1.2)$$

$$\langle \underset{\sim}{R}(0) \cdot \underset{\sim}{R}(t) \rangle = 6\xi m k_B T\, \delta(t) \qquad (4.2)$$

(along each coordinate, $\langle R_\alpha(0)\, R_\beta(t) \rangle = 2\xi m k_B T\, \delta(t)\, \delta_{\alpha\beta}$

$$\langle \underset{\sim}{R}(t) \cdot \underset{\sim}{v}(0) \rangle = 0 \qquad (\langle R_\alpha(t)\, v_\beta(0) \rangle = 0) \qquad (1.3)$$

$$\langle \underset{\sim}{R}(t) \cdot \underset{\sim}{F}(0) \rangle = 0 \qquad (\langle R_\alpha(t)\, F_\beta(0) \rangle = 0) \qquad (4.3)$$

All higher moments of $\underset{\sim}{R}(t)$ are set by its second moment.
For such an $\underset{\sim}{R}(t)$, if $\phi(t)$ is any function of time, the quantity

$$(\Delta\phi R_\alpha)^G \equiv \int_t^{t+\Delta t} \phi(t')\, R_\alpha(t')\, dt'$$

(Δt large relative to time scale of fluctuations of $\underset{\sim}{R}(t)$, small relative to ξ^{-1})

is a random variable following a Gaussian distribution, with mean $\langle (\Delta\phi R_\alpha)^G \rangle = 0$ and variance $\langle [(\Delta\phi R_\alpha)^G]^2 \rangle = 2m\xi k_B T \int_t^{t+\Delta t} \phi^2(t')\, d$

$(\Delta\phi R_\alpha)^G$ can be readily sampled, although $R_\alpha(t)$ cannot!

All numerical approaches rest upon integrating the Langevin equation over a small interval Δt.

Simple predictor algorithm (Ermak, 1976)

$\underset{\sim}{F}(\underset{\sim}{r}(t))/m$

$$\underset{\sim}{r}(t+\Delta t) = \underset{\sim}{r}(t) + \frac{1}{\xi \Delta t}\left(1 - e^{-\xi \Delta t}\right) \Delta t \, \underset{\sim}{v}(t) + \frac{1}{\xi \Delta t}\left[1 - \frac{1}{\xi \Delta t}\left(1 - e^{-\xi \Delta t}\right)\right] \Delta t^2 \, \underset{\sim}{a}(t) + \Delta \underset{\sim}{r}^G \tag{4.4}$$

$$\underset{\sim}{v}(t+\Delta t) = \underset{\sim}{v}(t)\, e^{-\xi \Delta t} + \frac{1}{\xi \Delta t}\left(1 - e^{-\xi \Delta t}\right) \Delta t \, \underset{\sim}{a}(t) + \Delta \underset{\sim}{v}^G \tag{4.5}$$

where $\Delta \underset{\sim}{r}^G$ (random displacement) and $\Delta \underset{\sim}{v}^G$ (random velocity change) are sampled from a set of three bivariate Gaussian distributions, with zero means, variances

$$\sigma_r^2 \equiv \left\langle \left(\Delta r_\alpha^G\right)^2 \right\rangle = (\Delta t)^2 \cdot \frac{k_B T}{m} \cdot \frac{1}{\xi \Delta t}\left[2 - \frac{1}{\xi \Delta t}\left(3 - 4e^{-\xi \Delta t} + e^{-2\xi \Delta t}\right)\right] \tag{4.6}$$

$$\sigma_v^2 \equiv \left\langle \left(\Delta v_\alpha^G\right)^2 \right\rangle = \frac{k_B T}{m}\left(1 - e^{-2\xi \Delta t}\right) \tag{4.7}$$

and covariance

$$C_{rv}\, \sigma_r \sigma_v = \Delta t \cdot \frac{k_B T}{m} \cdot \frac{1}{\xi \Delta t}\left(1 - e^{-\xi \Delta t}\right)^2 \tag{4.8}$$

For techniques to sample a set of correlated Gaussian random variables, see Allen and Tildesley, app. G.3.

Lacking a corrector step, the Ermak algorithm is second order in accuracy, and necessitates the use of a small Δt, i.e. $\xi \Delta t \ll 1$.

Verlet-type algorithms

Example:

$$\underset{\sim}{r}(t+\Delta t) = \underset{\sim}{r}(t) + \frac{1}{\xi\Delta t}\left(1-e^{-\xi\Delta t}\right)\Delta t\,\underset{\sim}{v}(t) + \frac{1}{\xi\Delta t}\left[1-\frac{1}{\xi\Delta t}\left(1-e^{-\xi\Delta t}\right)\right]\Delta t^2\,\underset{\sim}{a}(t) +$$

$$+\,\Delta\underset{\sim}{r}^G$$

$$\underset{\sim}{v}(t+\Delta t) = \underset{\sim}{v}(t)\,e^{-\xi\Delta t} + \frac{1}{\xi\Delta t}\left[\frac{1}{\xi\Delta t}\left(1-e^{-\xi\Delta t}\right) - e^{-\xi\Delta t}\right]\Delta t\;\underset{\sim}{a}(t) +$$

$$+\;\frac{1}{\xi\Delta t}\left[1-\frac{1}{\xi\Delta t}\left(1-e^{-\xi\Delta t}\right)\right]\Delta t\;\underset{\sim}{a}(t+\Delta t) + \Delta\underset{\sim}{v}^G \qquad (4.9)$$

Extension of Verlet algorithm to Brownian dynamics:
van Gunsteren, W.F.; Berendsen, H.J.C. Molec. Phys. 1982, 45, 637-647

Extension of Verlet leap-frog algorithm to Brownian Dynamics:
van Gunsteren, W.F.; Berendsen, H.J.C. Molec. Simul. 1988, 1, 173-185

Verlet-type algorithms afford the use of up to 10 times larger integration time steps than Ermak algorithm.

Verlet-type algorithms can be coupled to a SHAKE-type scheme for dealing with intramolecular constraints.

4.2. Integration in configuration space only.

In many problems, one is interested only in how the system will evolve in configuration space at long times.

Consider the Langevin equation,

$$m\,\dot{\underset{\sim}{v}}(t) = -m\,\xi\,\underset{\sim}{v}(t) + \underset{\sim}{F}(\underset{\sim}{r}) + \underset{\sim}{R}(t) \qquad (4.10)$$

in the limit of long time steps, $\Delta t >> 1/\xi$

- The relaxation time of the velocity is $\sim 1/\xi$. For $\Delta t >> 1/\xi$, no matter what $\underset{\sim}{v}(t)$ was, $\underset{\sim}{v}(t+\Delta t)$ will be sampling values from a Maxwell-Boltzmann (equilibrium) distribution.
- The evolution of $\underset{\sim}{r}(t)$ to its equilibrium distribution is much slower than that of $\underset{\sim}{v}(t)$. [For a free particle, $\underset{\sim}{r}(t)$ grows in an unbounded fashion]
- If we are interested in time scales $>> \frac{1}{\xi}$, an order of magnitude analysis of the two terms in (4.10) involving velocity gives:

$$|m\,\dot{\underset{\sim}{v}}(t)| \sim m\,\frac{|\Delta \underset{\sim}{v}|}{\Delta t} \sim m\,\frac{|\underset{\sim}{v}|}{\Delta t} << m\,\frac{|\underset{\sim}{v}|}{1/\xi} \sim |m\xi\,\underset{\sim}{v}(t)|$$

i.e. for $\Delta t >> 1/\xi$, the inertial term of eq (4.1) becomes insignificant relative to the friction term. ("high friction limit").

The Langevin equation can then be substituted by the "position Langevin equation" (adiabatic elimination of fast momentum variabl

$$\dot{\underset{\sim}{r}}(t) = \frac{\underset{\sim}{F}(t)}{m\xi} + \dot{\underset{\sim}{r}}^{\circ}(t) \qquad (4.11)$$

where $\dot{\underset{\sim}{r}}^{\circ}(t)$, a "random velocity process" is a white noise with autocorrelation function

$$\langle \dot{r}^{\circ}_{\alpha}(t)\, \dot{r}^{\circ}_{\beta}(0) \rangle = 2\,\frac{k_B T}{m\xi}\,\delta(t)\,\delta_{\alpha\beta} = 2D\,\delta(t)\,\delta_{\alpha\beta}$$

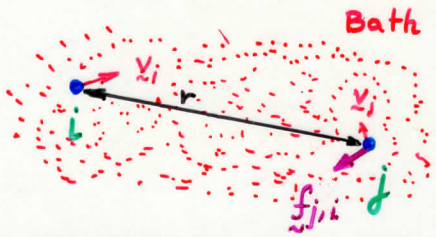
Numerical integration of (4.11):

$$\underset{\sim}{r}(t+\Delta t) = \underset{\sim}{r}(t) + \frac{1}{m\xi}\,\underset{\sim}{F}(t)\Delta t + \Delta \underset{\sim}{r}^{G} \qquad (4.12)$$

Components of $\Delta \underset{\sim}{r}^{G}$ selected independently from Gaussian distributions with zero mean and variance $\langle (\Delta r^{G}_{\alpha})^2 \rangle = 2D\Delta$

5. Systems of Interacting Brownian Particles

Hydrodynamic Interactions:



Motion of particle i modifies flow field (induces solvent flow)
This induced flow will exert a frictional (hydrodynamic) force on another particle j.
This hydrodynamic interaction decays only slowly with distance ($\propto \frac{1}{r}$ at large r)

CONSEQUENCE Friction coefficients ξ should depend on the positions and momenta of all particles.

SIMPLIFICATION Drop dependence of ξ on momenta, and concentrate on effects of configuration.

Smoluchowski equation for interacting Brownian particles:

$$\frac{\partial}{\partial t} p(\underset{\sim}{r}, t) + \sum_i \sum_j \underset{\sim}{\nabla}_{\underset{\sim}{r}_i} \cdot \frac{\underline{\underline{D}}_{ij}(\underset{\sim}{r})}{k_B T} \cdot \underset{\sim}{f}_j(\underset{\sim}{r}) p(\underset{\sim}{r}, t) =$$

p: probability density in config. space for all particles.

$\underline{\underline{D}}_{ij}$: 3×3 diffusion matrix for the pair of particles (i,j). Can be viewed as a submatrix of a $3N \times 3N$ diffusion matrix $\underline{\underline{D}}$. A function of configuration!

$\underset{\sim}{f}_j$: Force on j due to interaction with other particles and ext. fields $(-\nabla_{\underset{\sim}{r}_j} \mathcal{V})$

$$= \sum_i \sum_j \underset{\sim}{\nabla}_{\underset{\sim}{r}_i} \cdot \underline{\underline{D}}_{ij}(\underset{\sim}{r}) \cdot \underset{\sim}{\nabla}_{\underset{\sim}{r}_j} p(\underset{\sim}{r}, t) \qquad (5.1)$$

TERMINOLOGY

$\frac{\underline{\underline{D}}}{k_B T}$ = mobility matrix, $\underline{\underline{M}}$

$\underline{\underline{D}}^{-1} = \underline{\underline{R}}$ = resistance matrix

} depend on all particle positions.

(5.2)

Position-Langevin description of interacting Brownian particles:
(useful in Brownian Dynamics simulations)

$$\underset{\sim}{r}_i(t+\Delta t) = \underset{\sim}{r}_i(t) + \sum_j \frac{\underline{\underline{D}}_{ij}(\underset{\sim}{r})}{k_B T} \cdot \underset{\sim}{f}_j(\underset{\sim}{r})\,\Delta t + \nabla_{\underset{\sim}{r}_j} \cdot \underline{\underline{D}}_{ij}(\underset{\sim}{r})\,\Delta t + \Delta \underset{\sim}{r}_i^{\,G}$$

$\Delta \underset{\sim}{r}_i^{\,G}$: random displacement. Usually selected as Gaussian.

Properties of the random displacements $\Delta \underset{\sim}{r}_i^{\,G}$:
Selected from a multivariate Gaussian distribution, with (5.3)

$$\langle \Delta \underset{\sim}{r}_i^{\,G} \rangle = \underset{\sim}{0} \quad , \quad \langle \Delta \underset{\sim}{r}_i^{\,G}\, \Delta \underset{\sim}{r}_j^{\,G} \rangle = 2\, \underline{\underline{D}}_{ij}\, \Delta t \qquad (5.4)$$

(special sampling techniques required for the generation of such correlated random numbers. See Allen + Tildesley, Appendix G).

$\underline{\underline{D}}$ is obtainable, in principle, from macroscopic hydrodynamics.

It is known exactly for two spherical particles at all center-center separations (solution to Stokes flow problem).

Dominant behavior at long distances:

$$\underline{\underline{D}}_{ij} = \frac{k_B T}{3\pi\eta d}\,\underline{\underline{1}} \qquad (i=j)$$

(d: particle diameter)

$$\frac{k_B T}{8\pi\eta r_{ij}} \left(\underline{\underline{1}} + \frac{\underset{\sim}{r}_{ij}\,\underset{\sim}{r}_{ij}}{r_{ij}^2} \right) \qquad (i \neq j)$$

($\underset{\sim}{r}_{ij}$: interparticle distance vector)

Oseen Tensor

For current ideas on the calculation of hydrodynamic forces and their application to suspensions, see J.F. Brady and G. Bossis, Ann. Rev. Fluid Mech. 1988, 20, 111-157 (Stokesian Dynamics technique).

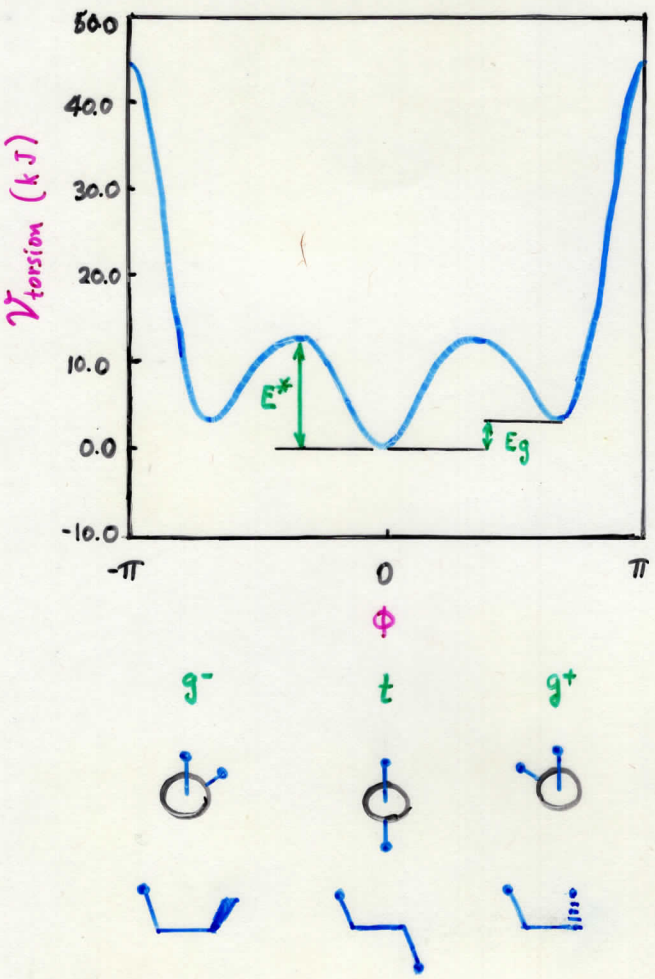
An example:

Brownian Dynamics Study of Polymer Conformational Transitions

Helfand, E.; Wasserman, Z.R.; Weber, T.A. Macromolecules 1980, 13, 526-533.
Helfand, E.; Wasserman, Z.R.; Weber, T.A. J.Chem.Phys. 1981, 75, 4441-4445.

THE PROBLEM

What is the mechanism of conformational isomerization of flexible polymer chains in solution?



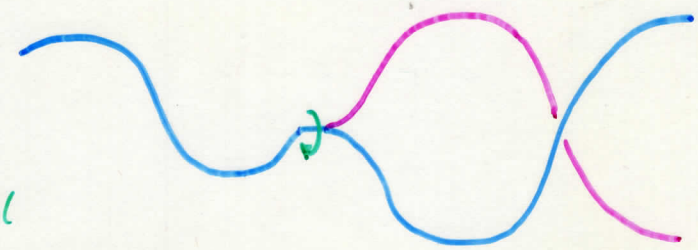
Torsional barrier $E^* = 3$ to $5\ k_B T$

Skeletal bonds spend most of their time in the vicinity of minima of the torsional potential, undergoing torsional oscillations.

Occasionally, they pass from the vicinity of one minimum (torsional state) to that of another minimum, by overcoming the energy barrier separating the minima.

Conformational transitions are "infrequent events".

- Rotation around single bond of a polymer in solution would be accompanied by an energetically expensive "thrashing" motion of chain tails.



∴ Conformational transitions must invdve cooperative motion of many bonds.

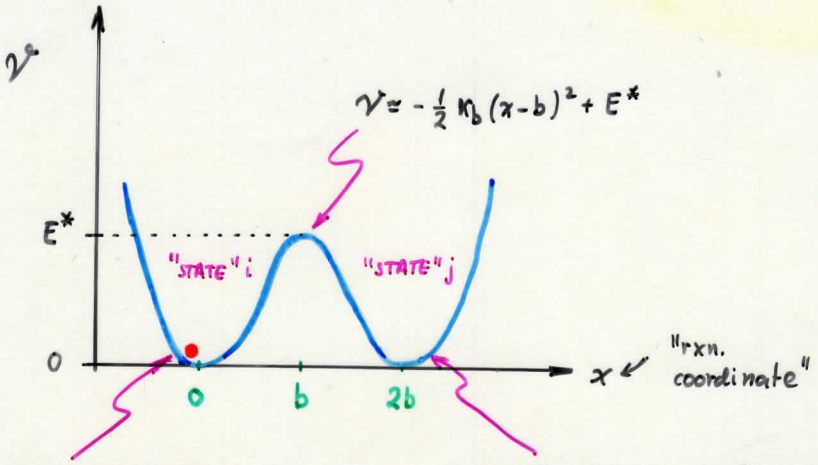
- Rotation around a single bond would imply activation energy ≃ E^* (E^* = trans-gauche barrier.)
  Simultaneous, "krankshaft"-like rotation around several consecutive bonds would imply an activation energy equal to a multiple of E^*.
  Is this observed?

- How does the flexibility (deformability) of bond lengths and bond angles around the rotating bond affect the conformational transition rate?

EXPERIMENTAL EVIDENCE (NMR, dielectric relaxation, ultrasonic attenuation, dynamic light scattering, fluorescence depolarization, excimer fluorescence)

- Characteristic time of relaxation processes in solution : 0.1 to 10 ns^{-1}!
- Rate varies inversely with the viscosity of the medium.
  (Brownian motion across a potential barrier in the high friction limit.
- Activation energy ≃ 20 kJ/mol. Of this, ~10 kJ/mol due to T-dependence of solvent viscosity. The remaining 10 kJ/mol is comparable to a single trans-gauche barrier.

A note on the Kramers model for rate processes.



Local description of the potential:

$\mathcal{V} = \frac{1}{2}\kappa_\omega x^2$

$\mathcal{V} = \frac{1}{2}\kappa_\omega (x-2b)^2$

Brownian particle moving across a potential energy barrier, E^* subject to interaction with a bath of temperature T and friction coefficient ξ.

Imagine ensemble of such particles, at equilibrium.

$$\text{Rate constant } k_{i\to j} = \frac{\text{Number of transitions State } i \to \text{State } j \text{ per unit time}}{\text{Number of systems with particle in state } i.} \qquad (6.1)$$

Microscopic reversibility (detailed balance) $k_{i\to j} P_i = k_{j\to i} P_j$ (6.2)

(P_i: equil. probability of being in state i.)

Result of Kramers analysis (1940) in the harmonic approximation:

$$k\ (= k_{i\to j}) = \nu_0 \left(\sqrt{\zeta^2+1} - \zeta\right) \exp\left(-\frac{E^*}{k_B T}\right) \qquad (6.3)$$

with $\nu_0 = \frac{1}{2\pi}\sqrt{\frac{\kappa_\omega}{m}}$ (natural frequency of oscillation in harmonic region of well)

$\zeta = \frac{1}{2}\xi\sqrt{\frac{m}{\kappa_b}}$ (dimensionless friction coefficient)

Low friction limit: $\zeta \ll 1$, $k = \nu_0 \exp\left(-\frac{E^*}{k_B T}\right)$ (Transition State Theory)

High friction limit: $\zeta \gg 1$, $k = \frac{\nu_0}{2\zeta}\exp\left(-\frac{E^*}{k_B T}\right) = \frac{1}{\xi}\frac{\sqrt{\kappa_\omega \kappa_b}}{m}\exp\left(-\frac{E^*}{k_B T}\right)$

(ξ: proportional to viscosity)

THE MODEL

- 200- carbon center ring chain (to make all bonds equivalent).
- Harmonic potentials for bond lengths and bond angles.
  (bond spring constants weakened by 2-3 orders of magnitude; bond angle constants weakened by a factor of 3, to reduce the stiffness of the numerical integration problem).
- Phantom chain; no intramolecular interaction apart from torsional potential.
- No pentane effect!  ($g^+ g^-$ conformation, highly unfavorable in reality, not disallowed here).
- Solvent represented by a Brownian bath. (Relative masses of segments/solvent alone would not justify this. It is assumed that connectivity along the chain makes polymer motions sluggish enough to justify time scale separation requirement).
- No hydrodynamic interactions
  (felt that they would not affect the relatively rapid process of conformational isomerization occuring locally along the chain).

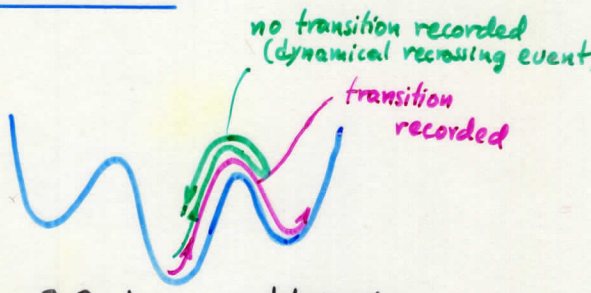
SIMULATION TECHNIQUE:

Numerical solution of the position Langevin equation (no inertial terms) for all chain atoms subject to torsional, friction, and random forces, with a Runge-Kutta method.

Friction coefficient $\xi = 10^{-5}$ ns^{-1} (establishes a time scale)

Integration time step $\Delta t = 5 \times 10^{-6}$ ns $= 5$ fs.

Interpretation of results: First passage time analysis.



Counting of well-to-well transitions only.

Overall rate for all transitions $\lambda = 2 P_t k_{t \to g} + 2 P_g k_{g \to t}$ obtained, and individual rate constants extracted by invoking detailed balance.

Determination of λ by Hazard Rate Analysis.

Let $F(t)$ = probability that a bond will undergo a transition in time t or less since its last transition.

Hazard rate $$h(t) = \frac{1}{1-F(t)} \frac{dF}{dt} \qquad (6.4)$$

$h(t)\,dt$ = probability that a bond, which underwent no transition for a time t since its last transition, has a transition between t and $t+dt$.

Cumulative hazard $$H(t) = \int_0^t h(t)\,dt. \qquad (6.5)$$

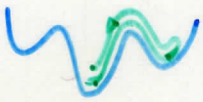
By definition, $$F(t) = 1 - e^{-H(t)} \qquad (6.6)$$

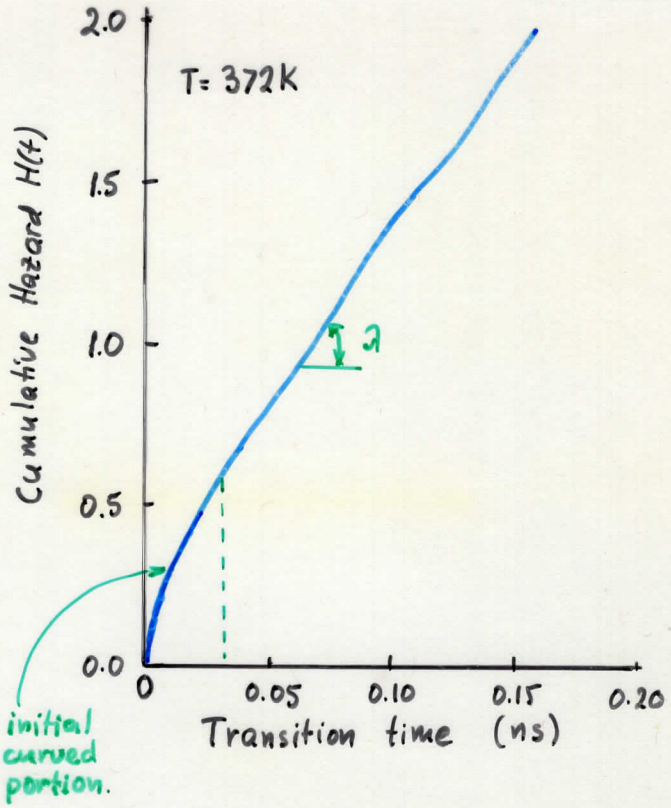
For a Poisson process (successive transitions of a bond uncorrelated),
$H(t) = \lambda t$, with λ = rate of conf. transitions. (6.7)

$H(t)$ can be accumulated very easily by recording the times it takes bonds to pass from a given state to an adjacent state. (See Nelson, W. Journal of Quality Control, 1969, 1, 27-52)

Findings:

- H(t) initially curved at short times. (Short-time rate appears enhanced.) This is because the short-time region is affected by angles that do not thermalize in destination state but quickly cross back into origin state.





- Long-time behavior linear, permits extracting a reliable rate constant λ.

Representative transition rates:

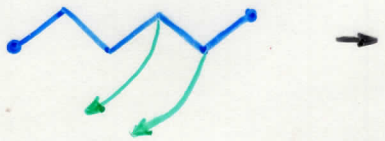
T(K)	λ_{tg} (ns^{-1})
425	7.7
372	4.6
330	2.5
297	1.5

(butane exhibits 29.6 ns^{-1})

- Activation energy extracted from simulations is slightly larger than one barrier height: $(1.12 \pm 0.02)\, E^*$. This eliminates the possibility of simultaneous transition of several bonds over barriers.

- There is cooperativity in the motion of neighboring torsion angles. Although one bond makes it over the barrier at a time, the neighboring bonds will undergo distortions that facilitate this.

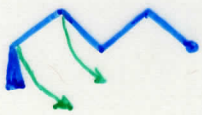
- There is correlation between the times of transition of neighboring bonds. Although transitions do not occur strictly simultaneously, immediately after a transition occurs there is an enhanced probability that another will occur in a nearby bond. (transitions of neighboring bonds occur within a few picoseconds from each other).
  Particularly strong correlation between second-neighbor bonds separated by a trans:
  Crank like counterrotational transitions:



t t t

$g^{\pm}\, t\, g^{\mp}$

"kink"



$g^{\pm}\, t\, t$

$t\, t\, g^{\pm}$

"gauche migration"

- The reaction coordinate in the neighborhood of the transition state is a localited mode. As the transforming bond rotates over the energy barrier, neighboring degrees of freedom undergo distortions, which are such as to lead to decreasing amounts of motion away from the center of action. Effectively, only a few neighboring degrees of freedom move.

- Increasing the stiffness of bond lengths and, more significantly, bond angles, decreases the rate of conformational isomerization. (40% decrease in trans-gauche rate with a tenfold increase in bond angle bending constant).