Brownian Motion, Langevin Dynamics, Harmonic Baths

Suppose you have a big solute particle hanging out in solution:

How does it move? What's the effect of solvent if you can't keep track of all the solvent molecules?

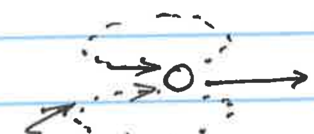
Drag & Brownian Motion

The Langevin equation:

$$m\ddot{x} = \underbrace{-\frac{\partial V(x)}{\partial x}}_{\text{force from potential}} - \underbrace{\xi}_{\text{friction}} \underbrace{\dot{x}(t)}_{\text{velocity}} + \underbrace{R(t)}_{\text{random force}}$$

We know that solvent sometimes responds to flow later:

Hydrodynamics



$\xi(t)$ can be negative!

That is friction due to hydrodynamic effects is

1) time dependent
2) Not always positive!

GLE:

$$m\ddot{x} = -\frac{\partial V}{\partial x} - \int_0^t d\tau\, \xi(t-\tau)\underbrace{\dot{x}(\tau)}_{\text{velocity at earlier times}} + R(t)$$

$\xi(t-\tau)$: friction kernel

$\xi(t)$ measures the effect of dynamic friction of a solvent

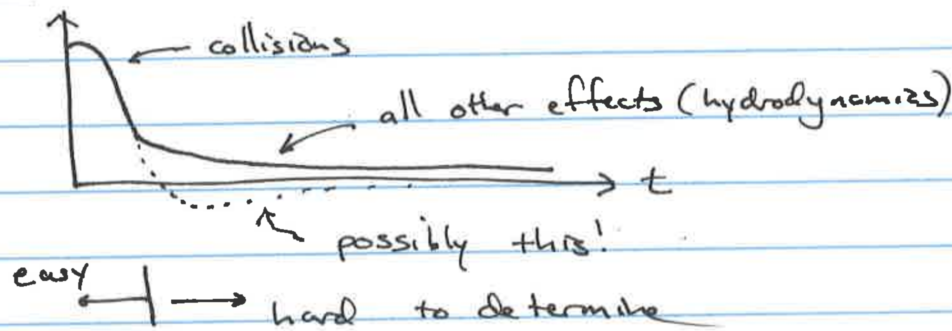
$\zeta(t)$ is necessary for viscoelastic solvents

$R(t)$ is a <u>fluctuating</u> <u>force</u> or Brownian motion often assumed to be a <u>Gaussian</u> random process: $\langle R(t)\,R(0)\rangle$ the second moment describes the properties exactly

$$\zeta(t) = \frac{1}{k_B T}\langle R(t)\cdot R(0)\rangle$$ is the 2^{nd} Fluctuation Dissipation Theorem

(The 1^{st} is <u>linear</u> <u>response</u> theory)

$\langle R(t)\cdot R(0)\rangle \leftarrow$ correlation of kicks by the solvent



Where does the GLE come from?

Let's assume the solvent is a <u>harmonic</u> <u>bath</u>:

$$\mathcal{H} = \underbrace{\frac{p^2}{2m} + V(x)}_{\text{system}} + \underbrace{H_B}_{\text{Bath}} + \underbrace{\Delta V(x, x_1, \ldots x_N)}_{\text{system-bath coupling}}$$

$$H_B = \sum_{\alpha=1}^{N} \frac{P_\alpha^2}{2m_\alpha} + \frac{1}{2} m_\alpha \omega_\alpha^2 x_\alpha^2 \leftarrow$$ a set of N Harmonic Oscillators (uncoupled!)

$$\Delta V = -\sum_{\alpha=1}^{N} g_\alpha x_\alpha x \quad \leftarrow \text{Bilinear system } (x) - \text{Bath} (x_\alpha) \text{ coupling.}$$

g_α is a coupling constant

$$H_B + \Delta V = \sum_{\alpha=1}^{N} \frac{p_\alpha^2}{2m_\alpha} + \underbrace{\frac{1}{2} m_\alpha \omega_\alpha^2 x_\alpha^2 - g_\alpha x_\alpha x}_{\text{let's complete the square}}$$

$$\frac{1}{2} m_\alpha \omega_\alpha^2 \left(x_\alpha^2 - \frac{2 g_\alpha}{m_\alpha \omega_\alpha^2} x x_\alpha \right)$$

$$= \frac{1}{2} m_\alpha \omega_\alpha^2 \left(x_\alpha - \frac{g_\alpha x}{m_\alpha \omega_\alpha^2} \right)^2 - \frac{g_\alpha^2 x^2}{2 m_\alpha \omega_\alpha^2}$$

$$H_B + \Delta V = \sum_{\alpha=1}^{N} \left[\frac{p_\alpha^2}{2m_\alpha} + \frac{1}{2} m_\alpha \omega_\alpha^2 \left(x_\alpha - \frac{g_\alpha}{m_\alpha \omega_\alpha^2} \right)^2 \right] - \underbrace{\sum_{\alpha=1}^{N} \frac{g_\alpha^2}{2 m_\alpha \omega_\alpha^2} x^2}_{\text{only system coordinate!}}$$

$$\mathcal{H} = \frac{p^2}{2m} + \underbrace{V(x) - \sum_{\alpha=1}^{N} \frac{g_\alpha^2}{2 m_\alpha \omega_\alpha^2} x^2}_{W(x) \text{ or potential of mean force}} + \sum_{\alpha=1}^{N} \left[\frac{p_\alpha^2}{2m_\alpha} + \frac{1}{2} m_\alpha \omega_\alpha^2 \left(x_\alpha - \frac{g_\alpha}{m_\alpha \omega_\alpha^2} \right)^2 \right]$$

We can get to the GLE by using Hamilton's equations:

$$m\ddot{x} = \dot{p} = -\frac{\partial \mathcal{H}}{\partial x}$$

$$m_\alpha \ddot{x}_\alpha = \dot{p}_\alpha = -\frac{\partial \mathcal{H}}{\partial x_\alpha}$$

$$m\ddot{x} = -\frac{\partial W(x)}{\partial x} - \sum_{\alpha=1}^{N} m_\alpha \omega_\alpha^2 \left(x_\alpha - \frac{g_\alpha}{m_\alpha \omega_\alpha^2} x\right) \frac{g_\alpha}{m_\alpha \omega_\alpha^2}$$

$$= \frac{-\partial W(x)}{\partial x} - \sum_{\alpha=1}^{N} g_\alpha \left(x_\alpha - \frac{g_\alpha}{m_\alpha \omega_\alpha^2} x\right)$$

$$m\ddot{x}_\alpha = -m_\alpha \omega_\alpha^2 \left(x_\alpha - \frac{g_\alpha}{m_\alpha \omega_\alpha^2} x\right)$$

$$\ddot{x}_\alpha = -\omega_\alpha^2 x_\alpha + \frac{g_\alpha}{m_\alpha} x$$

2^{nd} order diff eqs that are <u>coupled</u>

A brief interlude on <u>Laplace transforms</u>

$x(t)$ is a function of <u>time</u> t

$$L(x) \equiv \int_0^\infty x(t)\, e^{-pt}\, dt$$

Like a Real-valued fourier transform

Provable properties:

$$L(x+y) = L(x) + L(y)$$

$$L(ax) = a\,L(x)$$

$$L(\dot{x}) = pL(x) - p\,x(0)$$

$$L(\ddot{x}) = p^2 L(x) - p\,x(0) - \dot{x}(0)$$

$$L\left(\int_0^t g(t-\tau)\,h(\tau)\,d\tau\right) = G(p)\,H(p)$$

convolution theorem

Some important ones:

$$L(\cos at) = \frac{p}{p^2+a^2}$$

$$L(\sin at) = \frac{a}{p^2+a^2}$$

$$L(1) = \frac{1}{p}$$

What we're transforming

$$\ddot{x}_\alpha = -\omega_\alpha^2 x_\alpha + \frac{g_\alpha}{m_\alpha} x$$

$$m\ddot{x} = -\frac{\partial W(x)}{\partial x} - \sum_{\alpha=1}^{N} g_\alpha \left(x_\alpha - \frac{g_\alpha}{m_\alpha \omega_\alpha^2} x \right)$$

Bath first:

$$p^2 L(x_\alpha) - p\, x_\alpha(0) - \dot{x}_\alpha(0) = -\omega_\alpha^2 L(x_\alpha) + \frac{g}{m_\alpha} L(x)$$

$$(p^2 + \omega_\alpha^2) L(x_\alpha) = \frac{g_\alpha}{m_\alpha} L(x) + p\, x_\alpha(0) + \dot{x}_\alpha(0)$$

$$\boxed{L(x_\alpha) = \frac{\frac{g_\alpha}{m_\alpha} L(x) + p\, x_\alpha(0) + \dot{x}_\alpha(0)}{p^2 + \omega_\alpha^2}}$$

Then thee system coordinate:

$$mL(\ddot{x}) = -\frac{1}{p}\frac{\partial w(x)}{\partial x} - \sum_{\alpha=1}^{N} g_\alpha\left(L(x_\alpha) - \frac{g_\alpha}{m_\alpha \omega_\alpha^2}L(x)\right)$$

Substitute in $L(x_\alpha)$:

$$mL(\ddot{x}) = -\frac{1}{p}\frac{\partial w(x)}{\partial x} - \sum_{\alpha=1}^{N}\left[\frac{g_\alpha^2}{m_\alpha}\frac{1}{p^2+\omega_\alpha^2}L(x) + g_\alpha\frac{p}{p^2+\omega_\alpha^2}x_\alpha(0)\right.$$

$$\left. + g_\alpha \dot{x}_\alpha(0)\frac{1}{p^2+\omega_\alpha^2} - \frac{g_\alpha^2}{m_\alpha\omega_\alpha^2}L(x)\right]$$

Collect like terms:

$$mL(\ddot{x}) = \frac{-1}{p}\frac{\partial w(x)}{\partial x} - \sum_{\alpha=1}^{N}\frac{g_\alpha^2}{m_\alpha\omega_\alpha^2}\left[\frac{\omega_\alpha^2}{p^2+\omega_\alpha^2} - \frac{p^2+\omega_\alpha^2}{p^2+\omega_\alpha^2}\right]L(x)$$

$$+ g_\alpha x_\alpha(0)\frac{p}{p^2+\omega_\alpha^2} + g_\alpha\dot{x}_\alpha(0)\frac{1}{p^2+\omega_\alpha^2}$$

$$mL(\ddot{x}) = \frac{-1}{p}\frac{\partial w(x)}{\partial x} - \sum_{\alpha=1}^{N}\frac{g_\alpha^2}{m_\alpha\omega_\alpha^2}\left[\frac{-p}{p^2+\omega_\alpha^2}\right]\left(pL(x)\right) + g_\alpha x_\alpha(0)\frac{p}{p^2+\omega_\alpha^2}$$

$$+ \left(-px(0) + px(0)\right)\frac{g_\alpha^2}{m_\alpha\omega_\alpha^2}\frac{p}{p^2+\omega_\alpha^2} + \frac{g_\alpha\dot{x}_\alpha(0)}{\omega_\alpha}\frac{\omega_\alpha}{p^2+\omega_\alpha^2}$$

Inverse Laplace Transform:

$$m\ddot{x} = \frac{-\partial w(x)}{\partial x} - \sum_{\alpha=1}^{N}\left\{\frac{-g_\alpha^2}{m_\alpha\omega_\alpha^2}\int_0^t \cos(\omega_\alpha t)\,\dot{x}(t-\tau)\,d\tau\right.$$

$$+ g_\alpha x_\alpha(0)\cos(\omega_\alpha t) + \frac{g_\alpha^2 x(0)}{m_\alpha\omega_\alpha^2}\cos(\omega_\alpha t)$$

$$\left. + \frac{g_\alpha}{\omega_\alpha}\dot{x}_\alpha(0)\sin(\omega_\alpha t)\right]$$

$$m\ddot{x} = \frac{-\partial w(x)}{\partial x} - \int_0^t\left(\sum_{\alpha=1}^{N}\left(\frac{-g_\alpha^2}{m_\alpha\omega_\alpha^2}\right)\cos\omega_\alpha t\right)\dot{x}(t-\tau)\,d\tau$$

$$+ \sum_\alpha\left[\left\{g_\alpha x_\alpha(0) - \frac{g_\alpha^2 x(0)}{m_\alpha\omega_\alpha^2}\right\}\cos\omega_\alpha t + \frac{g_\alpha\dot{x}_\alpha(0)}{\omega_\alpha}\sin\omega_\alpha t\right]$$

So we've arrived at the GLF with:

$$\xi(t) = \sum_{\alpha=1}^{N} \left(\frac{-g_\alpha^2}{m_\alpha \omega_\alpha^2}\right) \cos \omega_\alpha t$$

$$R(t) = \sum_{\alpha=1}^{N} \left(g_\alpha x_\alpha(0) - \frac{g_\alpha^2}{m_\alpha \omega_\alpha^2} x(0)\right) \cos(\omega_\alpha t) + \frac{\dot{x}_\alpha(0) g_\alpha}{\omega_\alpha} \sin(\omega_\alpha t)$$

(1) If our bath is infinite, we can use an integral over the spectral density: $J(\omega) = \frac{-g_\alpha^2}{m_\alpha}$

$$\sum_{\alpha=1}^{N} \frac{-g_\alpha^2}{m_\alpha} = \int_0^\infty J(\omega)\, d\omega$$

$$\xi(t) = \int_0^\infty \frac{J(\omega)}{\omega^2} \cos(\omega t)\, d\omega$$

(2) The "Random" forces depend only on initial conditions of the coordinates $x(0)$, $x_\alpha(0)$, $\dot{x}_\alpha(0)$:

$$R(t) = \sum_{\alpha=1}^{N} \left\{ \left(g_\alpha x_\alpha(0) - \frac{g_\alpha^2}{m_\alpha \omega_\alpha^2} x(0)\right) \cos \omega_\alpha t + \dot{x}_\alpha(0) \frac{g_\alpha}{\omega_\alpha} \sin(\omega_\alpha t) \right\}$$

To connect everything together, we define a new set of "phase-shifted" coordinates:

$$q_\alpha(t) = x_\alpha(t) - \frac{g_\alpha}{m_\alpha \omega_\alpha^2} x(0)$$

$$\dot{q}_\alpha(t) = \dot{x}_\alpha(t)$$

$$\therefore R(t) = \sum_\alpha g_\alpha q_\alpha(t)$$

Since the q_α coordinates are <u>uncoupled</u> harmonic oscillators, we can use the Harmonic Oscillator partition function (or Gaussian integrals) to find:

$$\langle q_\alpha^2 \rangle = \frac{k_B T}{m_\alpha \omega_\alpha^2}$$

and: $\langle q_\alpha(t)\, q_\alpha(0) \rangle = \langle q_\alpha(0)^2 \rangle \cos(\omega_\alpha t)$

and: $\langle q_\alpha(t)\, q_\beta(0) \rangle = \langle q_\alpha(t)\, q_\alpha(0) \rangle \delta_{\alpha\beta}$

So to correlate the Random forces:

$$\langle R(t) \cdot R(0) \rangle = \left\langle \left(\sum_\alpha g_\alpha q_\alpha(t) \right) \left(\sum_\beta g_\beta q_\beta(0) \right) \right\rangle$$

$$= \sum_\alpha \sum_\beta g_\alpha g_\beta \langle q_\alpha(t)\, q_\beta(0) \rangle$$

$$= \sum_\alpha \sum_\beta g_\alpha g_\beta \langle q_\alpha(t)\, q_\alpha(0) \rangle \delta_{\alpha\beta}$$

$$= \sum_\alpha g_\alpha^2 \langle q_\alpha(0)^2 \rangle \cos \omega_\alpha t$$

$$= \left(\sum_\alpha \frac{g_\alpha^2}{m_\alpha \omega_\alpha^2} \cos \omega_\alpha t \right) k_B T$$

$$= k_B T\, \xi(t)$$

$$\therefore \quad \boxed{\xi(t) = \frac{1}{k_B T} \langle R(t) \cdot R(0) \rangle} \leftarrow$$

2nd Fluctuation Dissipation theorem!

What we know so far:

$$m\ddot{x} = \frac{-\partial W(x)}{\partial x} - \int_0^t \zeta(t)\,\dot{x}(t-\tau)\,d\tau + R(t)$$

$$\zeta(t) = \int_0^\infty \frac{J(\omega)}{\omega^2}\cos\omega t\,d\omega$$

$$\langle R(t)\cdot R(0)\rangle = k_B T\,\zeta(t)$$ ← exact for Harmonic Bath!

Applications of the GLE:

Static Friction:

$$\zeta(t) = \zeta_0\,\delta(t)$$

$$\langle R(t)\cdot R(0)\rangle = k_B T\,\zeta_0\,\delta(t) = \frac{k_B T \zeta_0}{2\,dt}$$

This Recovers the Langevin Equation with Static Friction but requires a random force that is truly random (ie. uncorrelated at later times). This is not very realistic!

The Sluggish Bath:

$$\zeta(t) = \zeta_0$$

$$\int_0^t \dot{x}(t-\tau)\,\zeta_0\,d\tau \equiv \int_0^t \zeta_0\,\dot{x}(t')\,dt'$$

$$= \zeta_0\left(x(t) - x(0)\right)$$

This is a form of Dynamic Caging

$$m\ddot{x} = \frac{-\partial}{\partial x}\left[W(x) + \frac{1}{2}\zeta_0(x-x_0)^2\right] + R(t)$$

Sluggish Baths confine system coordinates!

How to get the spectral density:

$$I(\omega) = \int_{-\infty}^{\infty} \langle v(t) \cdot v(0) \rangle e^{i\omega t} \, dt$$

We still need a model for how bath modes of a specific frequency interact with the system coordinate

---

If we have an isotropic fluid (with an atom moving through the fluid), at equilibrium, there is no net force on the particle, so

$$\frac{\partial w(x)}{\partial x} = 0$$

$\therefore$

$$m\ddot{x}(t) = -\int_0^t d\tau \, \zeta(t-\tau)\, \dot{x}(\tau) + R(t)$$

$$m\dot{v}(t) \qquad\qquad \dot{x}(\tau) = v(\tau)$$

Now multiply through by the initial velocity $v(0)$:

$$m \frac{d}{dt} v(t)\, v(0) = -\int_0^t d\tau \, \zeta(t-\tau)\, v(0)\, v(\tau) + v(0)\, R(t)$$

Now, let's average over initial conditions:

$$m \frac{d}{dt} \langle v(t)\, v(0) \rangle = -\int_0^t \zeta(t-\tau) \langle v(0)\, v(\tau) \rangle + \langle v(0) R(t) \rangle$$

random

$$\dot{C}_{vv}(t) = -\int_0^t \gamma(t-\tau)\, C_{vv}(\tau)\, d\tau$$

$$\gamma(t) = \zeta(t)/m$$

Using Laplace transforms:

$$p\,L[C_{vv}] - C_{vv}(0) = -L[\gamma]\,L[C_{vv}]$$

$$\therefore \quad L[C_{vv}] = \frac{C_{vv}(0)}{p + L[\gamma]}$$

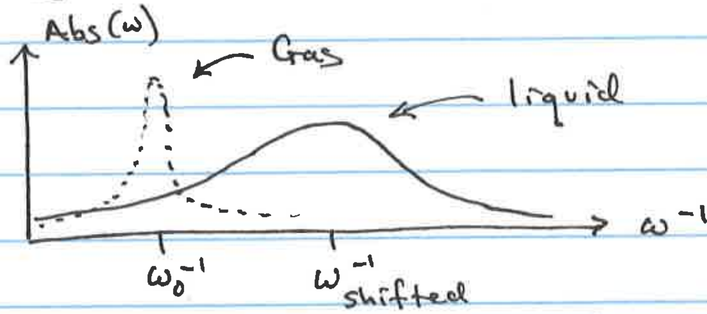
In the static friction limit, $\zeta(t) = \zeta_0\,\delta(t)$
and $L[\gamma] = \gamma$

$$\therefore \quad L[C_{vv}] = \frac{C_{vv}(0)}{p+\gamma}$$

$$\therefore \quad C_{vv}(t) = \underbrace{C_{vv}(0)}_{= \langle v^2 \rangle = \frac{k_B T}{m}}\, e^{-\gamma t}$$

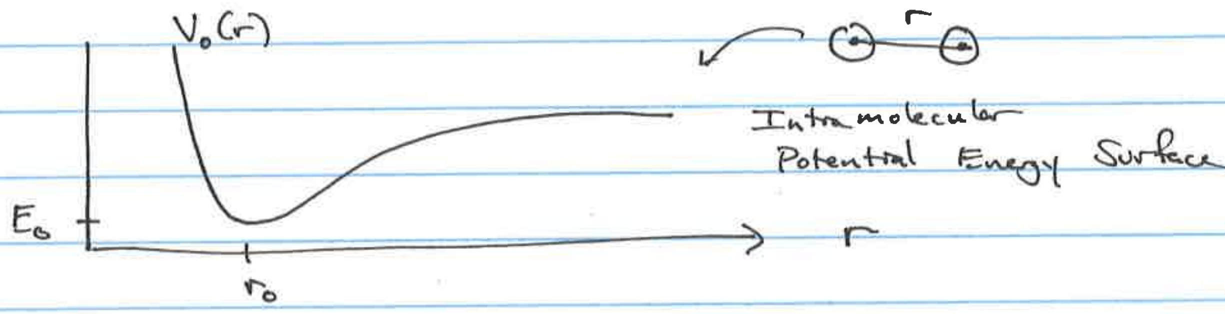
$\therefore$ Static Friction $\Rightarrow$ velocity correlation functions decay exponentially!

Vibrating Molecules in a Liquid



1) Condensed phase causes absorption frequency to shift
2) width of line $\Rightarrow$ relaxation rate = higher in liquid

How do we get there?

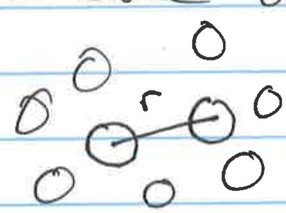


$$\Delta r = r(t) - r_0$$

Abs(ω) $\propto$ Fourier Transform of $\langle \Delta r(0)\, \Delta r(t) \rangle$

Why? (Dipole $\propto$ bond length)

The same diatomic in a liquid:



The spectral shifts are almost always due to anharmonicity

$$V_0(r) = E_0 + \frac{1}{2} m \omega_0^2 (r-r_0)^2 - \frac{g}{6}(r-r_0)^3 + \cdots$$

g = anharmonicity constant

When interacting with a solvent, some things change with Δr

1) Dipole (changes coupling to local field E)
2) Volume (changes short range repulsive forces between liquid & molecule)

excluded volume effects

$$V_{interaction} = -\mu(r)\,\underbrace{E}_{\text{electric field}} - \eta(r)\,\underbrace{F}_{\text{field due to repulsive forces (positive)}}$$

Things we know:

$\frac{d\mu}{dr} > 0$ i.e. Dipole gets bigger with bigger r

$\frac{d\eta}{dr} < 0$ excluded volume effects are overall bigger & more positive with increasing r

If both E & F are governed by Gaussian statistics:

$W(r)$ in Langevin approach has squared contributions to potential

$$\bar{V}(r) = V_0(r) \underbrace{- \frac{\mu^2 \beta \langle E^2\rangle}{2} - \frac{\eta^2 \beta \langle F^2\rangle}{2}}_{\text{equipartition for Gaussian distributed things}}$$

$$\frac{d\bar{V}}{dr} = m\omega_0^2(r-r_0) - \frac{g}{2}(r-r_0)^2 - \mu\frac{d\mu}{dr}\beta\langle E^2\rangle - \eta\frac{d\eta}{dr}\langle F^2\rangle$$

At the new minimum, $\frac{d\bar{V}}{dr} = 0$

At the old minimum, $\frac{dV_0(r)}{dr} = 0 \implies r_0$

$$0 = m\omega_0^2 (r_{eq} - r_0) - \frac{g}{2}(r_{eq} - r_0)^2 - \frac{d\ln\mu}{dr}\mu^2\beta\langle E^2\rangle$$

$$- \frac{d\ln\eta}{dr}\eta^2\beta\langle F^2\rangle$$

$$r_{eq} - r_0 \cong \frac{1}{m\omega_0^2}\left[\frac{d\ln\mu}{dr}\mu^2\beta\langle E^2\rangle + \frac{d\ln\eta}{dr}\eta^2\beta\langle F^2\rangle\right]$$

$\therefore$ potential minimum is <u>shifted</u>

$$\frac{1}{m}\tilde{V}''(r_{eq}) = \omega_{eff}^2 = \omega_0^2 - \frac{g}{m}(r_{eq} - r_0)$$

linear solvent response causes a <u>shift</u> in equilibrium r, and this <u>shift</u> causes a frequency shift.