10.34, Numerical Methods Applied to Chemical Engineering
Professor William H. Green
Lecture #31: Fluctuation – Dissipation Theorem.

Fluctuation – Dissipation Theorem

Nobel Prize: Einstein 1905

Drag ~ Brownian motion → Diffusion

We say "flux" – But each particle is moving on its own. Only when we consider their movement over time can we consider there to be flux in a room.

This applies in lots of other physical situations

- coupling between work and heat

$$D = \frac{k_B T}{\zeta} \qquad \underline{F}_{drag} = -\zeta \underline{v} \qquad < \underline{v} >_{ter\,min\,al} = \frac{\underline{F}_{ext}}{\zeta}$$

$$< (\delta x)^2 >= 2Dt = \frac{2k_B T}{\zeta} t \qquad D\zeta = k_B T$$

v = velocity, ζ = drag coefficient

Johnson Noise

$$< (\delta V)^2 >= 2k_B T R(\omega) \frac{\Delta\omega}{\pi}$$

$$< (\delta I)^2 > R^2 = 2k_B T R(\omega) \frac{\Delta\omega}{\pi}$$

V = voltage, R = resistance,

$$< (\delta I)^2 >= \frac{2k_B T}{R(\omega)} \frac{\Delta\omega}{\pi} \qquad \{V = IR\}$$

Δω = bandwidth of voltmeter

Exxon Example

Find best lubricant

To find viscosity:

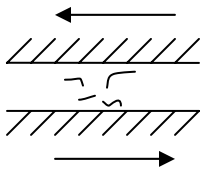

Figure 1. Fluid under shear.

shear on computer

1/shear rate < $\tau_{simulator}$

not a good way to calculate viscosity because τ is small so shear rate is high, which results in shear thinning and an irrelevant viscosity calculation

More practical way to do experiment:

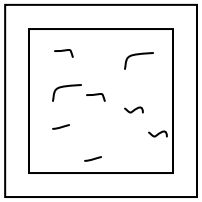

Figure 2. Fluctuation-dissipation on static system.

Use fluctuation – dissipation on static system to calculate diffusivity and then use Stokes – Einstein to obtain viscosity.

Use molecular dynamics for 10 ns or faster. Diffusion of orientation faster than diffusion of center of mass.

How to get time-dependent quantity? M. D. for 10 nanoseconds

$^{d}/_{dt}\, p(\ ) = \hat{O}[p(\ )]$

Master Equation

$$\frac{d}{dt} p_i(E) = -Z_{collision} p_i(E) - \sum_j k_{i\to j}(E) p_i(E) + Z_{collision} \int P_{E'\to E} p_i(E') dE' + k_{i\to j}(E) p_j(E)$$

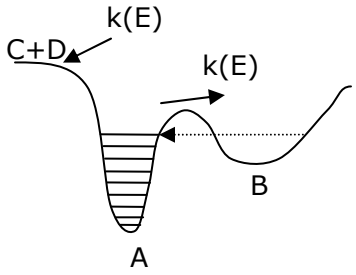

Figure 3. Energy diagram.

k(T,P) since $Z_{collision}$ depends on P

as P → ∞ → Boltzmann p(ε) → k(T)

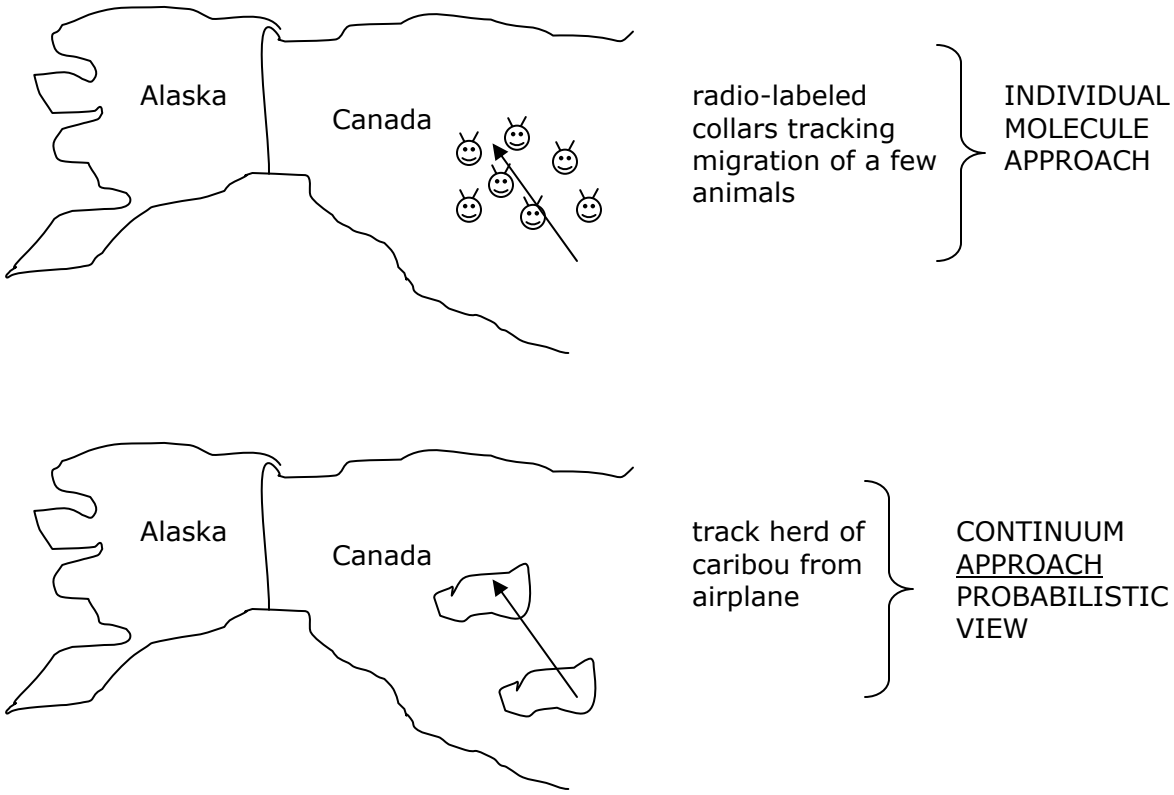

Figure 4. Two methods for tracking caribou as a way to compare the individual molecule to the continuum approach.

Individual Molecule Approach (Stochastic)

Gillespie Algorithm for Kinetic Monte Carlo

$$\frac{1}{\tau_{total}} = k_{dissociate}(\varepsilon) + k_{isomerization}(\varepsilon) + Z_{collision}$$

$$\tau_{change} = \tau_{total}(-\ln(rand))$$

if rand #2 < $\frac{k_{dissoc}}{k_{dissoc} + k_{isom} + Z}$ → molecule dissociated

if $\frac{k_{dissoc} + k_{isom}}{k_{dissoc} + k_{isom} + Z}$ > rand #2 > $\frac{k_{dissoc}}{k_{dissoc} + k_{isom} + Z}$ → molecule isomerized

else molecule underwent an energy-changing collision

Variance

$$\frac{\sigma}{f} \sim \sqrt{\frac{1-f}{N_{traj} f}}$$ if low-probability event (f is small), variance is BIG → no good

Alternative: solve master equation deterministically by discretizing.

$X_{in} = p_i(E_n)$ discrete $\{E_n\}$

$$\int \delta(E - E_n) \frac{d}{dt} p_i(E) dE = ...$$