Finite time corrections for normal diffusion in periodic potentials and diffusivities

David Dean
Laboratoire d'Ondes et Matière d'Aquitaine,
Université de Bordeaux

In collaboration with: **Gleb Oshanin**, LPTMC, UPMC Paris
Thomas Guerin, LOMA, Université de Bordeaux

Plan of talk

Diffusion in media with spatially varying potentials and diffusivities

Kubo type formulae for mean squared displacement for varying diffusivity

Results for varying diffusivity in one dimension

Results for periodic potentials in one dimension

Diffusion with spatially varying diffusivity

Fokker Planck Equation

$$\frac{\partial p(\mathbf{x},t)}{\partial t} = \nabla \cdot \kappa(\mathbf{x}) \nabla p(\mathbf{x},t)$$

Stochastic differential Equation - Ito

$$d\mathbf{X}_t = \sqrt{2\kappa(\mathbf{X}_t)}d\mathbf{B}_t + \nabla\kappa(\mathbf{X}_t)dt$$

Time dependent diffusion constant defined via MSD

$$\langle(\mathbf{X}_t - \mathbf{X}_0)^2\rangle = 2dD(t)t$$

Late time or effective diffusion constant

$$D_e = \lim_{t\to\infty} D(t)$$

Late time or effective diffusion constant

Use equivalence between self and collective diffusion constants for noninteracting tracers

Effective diffusion constant $$D_e\overline{\nabla p} = \overline{\mathbf{j}} = \overline{\kappa\nabla p}$$ Steady state diffusion equation

Effective dielectric constant $$\epsilon_e\overline{\nabla\phi} = \overline{\mathbf{D}} = \overline{\epsilon\nabla\phi}$$ Equation for electric displacement

Effective conductivity $$-\sigma_e\overline{\nabla\phi} = \overline{\mathbf{j}} = -\overline{\sigma\nabla\phi}$$ Ohm's law

Effective permeability $$\kappa_e\overline{\nabla P} = \overline{\mathbf{u}} = -\overline{\kappa\nabla\phi}$$ Darcy's law

Spatial averaging $$\overline{\cdots} = \frac{1}{V}\int_V d\mathbf{x}\ \cdots$$

For d> 1 difficult problem – studies date from Maxwell and Rayleigh

Diffusivity in one dimension

$$D_e = \overline{\frac{1}{\kappa}}^{-1}$$

Harmonic mean – capacitors and resistors in series

Can use steady state method or mean first passage time to distance L fixed then

$$L^2 = 2D_eT(L)$$

Equivalence of ensembles in large L, t limit

$$\nabla \cdot \kappa \nabla T(x) = -1$$

Not alway clear when this will work

FPT starting from x

In general in any dimension we have the bounds

$$\frac{1}{\kappa}^{-1} \leq D_e \leq \overline{\kappa}$$

Temporal behavior of D(t)

Equilibrium distribution given by $p_{eq}(x) = \frac{1}{V}$

(Large but finite system, periodic boundary conditions)

At small times sde is is dominated by diffusion (over drift)

$$\langle dX_t^2 \rangle = \langle 2\kappa(X_t) \rangle dt = 2dt \times \int dx \ \kappa(x) p_{eq}(x)$$

$$D(0) = \overline{\kappa}$$

$$\lim_{t \to \infty} D(t) = D_e = \overline{\kappa^{-1}}^{-1} < D(0)$$

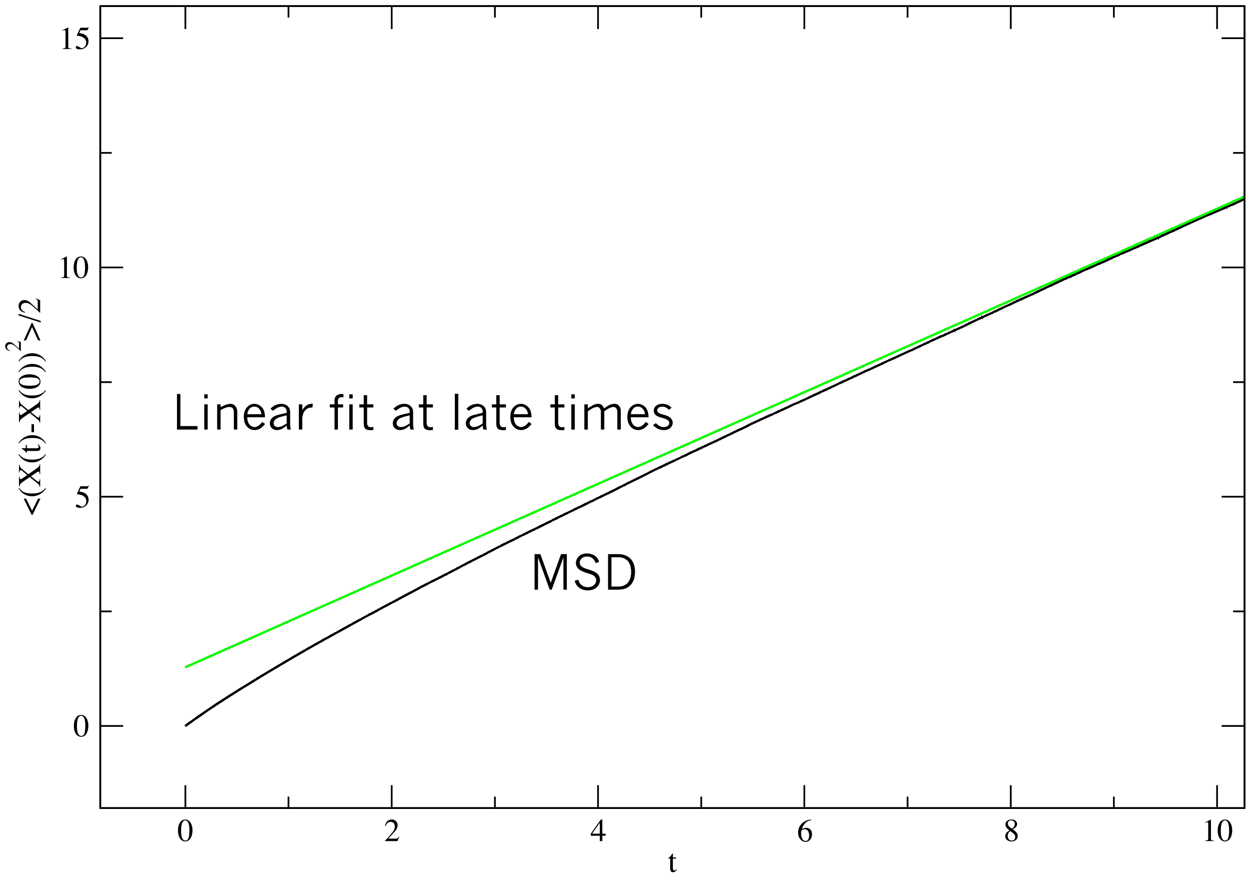
How does D(t) decay to its asymptotic value ?

Numerical simulation MSD

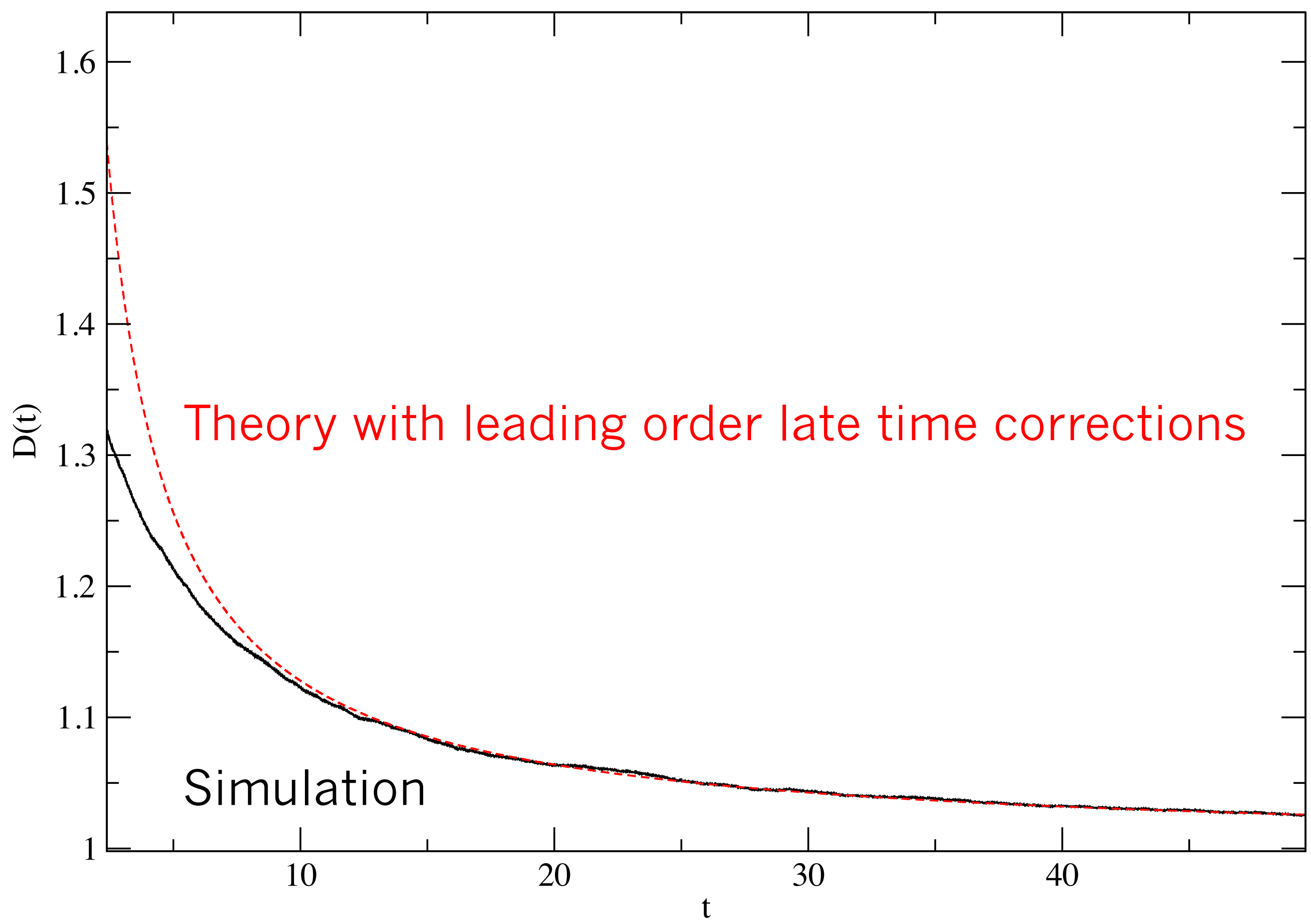
$$\kappa(x) = \frac{\kappa_0}{1 + \alpha \cos(\frac{2\pi x}{l})}$$

$$l = 4\pi$$

$$\alpha = 0.8$$



Behavior of D(t)



Kubo formula for periodically varying diffusivity

Integrate sde $\mathbf{X}_t - \mathbf{X}_0 = \int_0^t ds\ \sqrt{2\kappa(\mathbf{X}_s)} d\mathbf{B}_s + \int_0^t ds\ \nabla\kappa(\mathbf{X}_s)$

Square and rearrange

$$\langle (\mathbf{X}_t - \mathbf{X}_0)^2 - 2(\mathbf{X}_t - \mathbf{X}_0) \cdot \int_0^t ds\ \nabla\kappa(\mathbf{X}_s) + \int_0^t \int_0^t dsds'\ \nabla\kappa(\mathbf{X}_s) \cdot \nabla\kappa(\mathbf{X}_{s'}) \rangle$$

$$= \langle \int_0^t \int_0^t dsds'\ \sqrt{2\kappa(\mathbf{X}_s)} \sqrt{2\kappa(\mathbf{X}_{s'})} d\mathbf{B}_s \cdot d\mathbf{B}_{s'} \rangle$$

Initial conditions – equilibrium over very large system V composed of (N) elementary periodic cells Ω

$\mathbf{Y} = \mathbf{X} \mod \Omega$ is in equilibrium $p_0(\mathbf{y}) = \frac{1}{|\Omega|}$

$$p_0(\mathbf{x}) = \frac{1}{N|\Omega|}$$

In principle MSD saturates for a finite system but take system size much larger than distance diffused to observe late time diffusion constant

Detailed balance property

$$Hf(\mathbf{x}) = -\int d\mathbf{y}\nabla \cdot \kappa(\mathbf{x})\nabla\delta(\mathbf{x}-\mathbf{y})f(\mathbf{y})$$

Fokker Planck operator

$$H = H^{\dagger}$$

self adjoint

$$\frac{\partial p}{\partial t} = -Hp \qquad p(\mathbf{x},\mathbf{y},0) = \delta(\mathbf{x}-\mathbf{y})$$

Fokker Planck equation for transition density

Formal operator solution for transition density

$$p(\mathbf{x},\mathbf{y},t) = \exp(-tH)(\mathbf{x},\mathbf{y})$$

$$p(\mathbf{x},\mathbf{y},t) = p(\mathbf{y},\mathbf{x},t)$$

Transition density symmetric

The cross term

$$\langle (\mathbf{X}_t - \mathbf{X}_0) \cdot \int_0^t ds \; \nabla\kappa(\mathbf{X}_s) \rangle =$$

$$\int_0^t ds \int d\mathbf{x} d\mathbf{y} d\mathbf{x}_0 \; p(\mathbf{x},\mathbf{y};t-s) p(\mathbf{y},\mathbf{x_0};s) p_0(\mathbf{x}_0) \mathbf{x} \cdot \nabla\kappa(\mathbf{y}) - \int d\mathbf{y} d\mathbf{x}_0 \; p(\mathbf{y},\mathbf{x_0};s) p_0(\mathbf{x}_0) \mathbf{x_0} \cdot \nabla\kappa(\mathbf{y})$$

only appearance of $\mathbf{x_0}$

$$\langle (\mathbf{X}_t - \mathbf{X}_0) \cdot \int_0^t ds \; \nabla\kappa(\mathbf{X}_s) \rangle$$

$$= \int_0^t ds \int d\mathbf{x} d\mathbf{y} \; p(\mathbf{x},\mathbf{y};t-s) p_0(\mathbf{y}) \mathbf{x} \cdot \nabla\kappa(\mathbf{y}) - \int d\mathbf{y} d\mathbf{x}_0 \; p(\mathbf{y},\mathbf{x_0};s) p_0(\mathbf{x}_0) \mathbf{x_0} \cdot \nabla\kappa(\mathbf{y})$$

Change $\mathbf{x}$ to $\mathbf{x}_0$

Write s'=t-s

$$= 0$$

by symmetry of p(x,y,t)

The squared drift term

By defintion $\kappa(\mathbf{X}_t) = \kappa(\mathbf{Y}_t)$

Y has same Fokker Planck equation as X but where H acts on functions on Ω with periodic boundary conditions

$$\langle \int_0^t \int_0^t ds ds' \, \nabla\kappa(\mathbf{X}_s) \cdot \nabla\kappa(\mathbf{X}_{s'}) \rangle = 2\int_0^t ds \int_0^s ds' \int_\Omega d\mathbf{x} d\mathbf{y} \; p(\mathbf{x}, \mathbf{y}; s - s') p_0(\mathbf{y}) \nabla\kappa(\mathbf{x}) \cdot \nabla\kappa(\mathbf{y})$$

$$= 2\int_0^t ds \int_0^s ds' \int_\Omega d\mathbf{x} d\mathbf{y} \; \exp\left(-(s-s')H\right)(\mathbf{x}, \mathbf{y}) p_0(\mathbf{y}) \nabla\kappa(\mathbf{x}) \cdot \nabla\kappa(\mathbf{y})$$

Eigenfunction expansion of H on Ω

$$\exp(-tH)(\mathbf{x}, \mathbf{y}) = \frac{1}{|\Omega|} + \sum_{\lambda > 0} \exp(-\lambda t) \psi_\lambda(\mathbf{x}) \psi_\lambda(\mathbf{y})$$

$$\psi_0(\mathbf{x}) = \frac{1}{\sqrt{|\Omega|}}$$

Gives no contribution due to periodicity of κ

$$= \frac{2}{|\Omega|} \int_\Omega d\mathbf{x} d\mathbf{y} \left[tH'^{-1}(x, y) - H'^{-2}(x, y) + H'^{-2} \exp(-tH') \right] \nabla\kappa(\mathbf{x}) \cdot \nabla\kappa(\mathbf{y})$$

Where H' denotes the operator H acting on the subspace of functions orthogonal to the zero eigenvalue eigenfunction

H'^{-1} pseudo Green's function

The right hand side

$$\langle 2\kappa(\mathbf{X}_s)[d\mathbf{B}_s]^2\rangle = 2\overline{\kappa}ds$$

Off diagonal contributions are zero
Ito convention

$$\overline{\kappa} = \frac{1}{|\Omega|}\int_\Omega d\mathbf{x}\ \kappa(\mathbf{x})$$

Putting everything together

$$D(t) = \overline{\kappa} - \frac{1}{|\Omega| d}\int_\Omega d\mathbf{x}d\mathbf{y} H'^{-1}(x,y)\nabla\kappa(\mathbf{x})\cdot\nabla\kappa(\mathbf{y}) + \frac{1}{\Omega t}\int_\Omega d\mathbf{x}d\mathbf{y}\left[H'^{-2}(x,y) - H'^{-2}\exp(-tH')(x,y)\right]\nabla\kappa(\mathbf{x})\cdot$$

$$D_e$$

Transients

$$D(t) = D_e + \frac{C}{t}$$

Exponentially decaying terms gap in H’

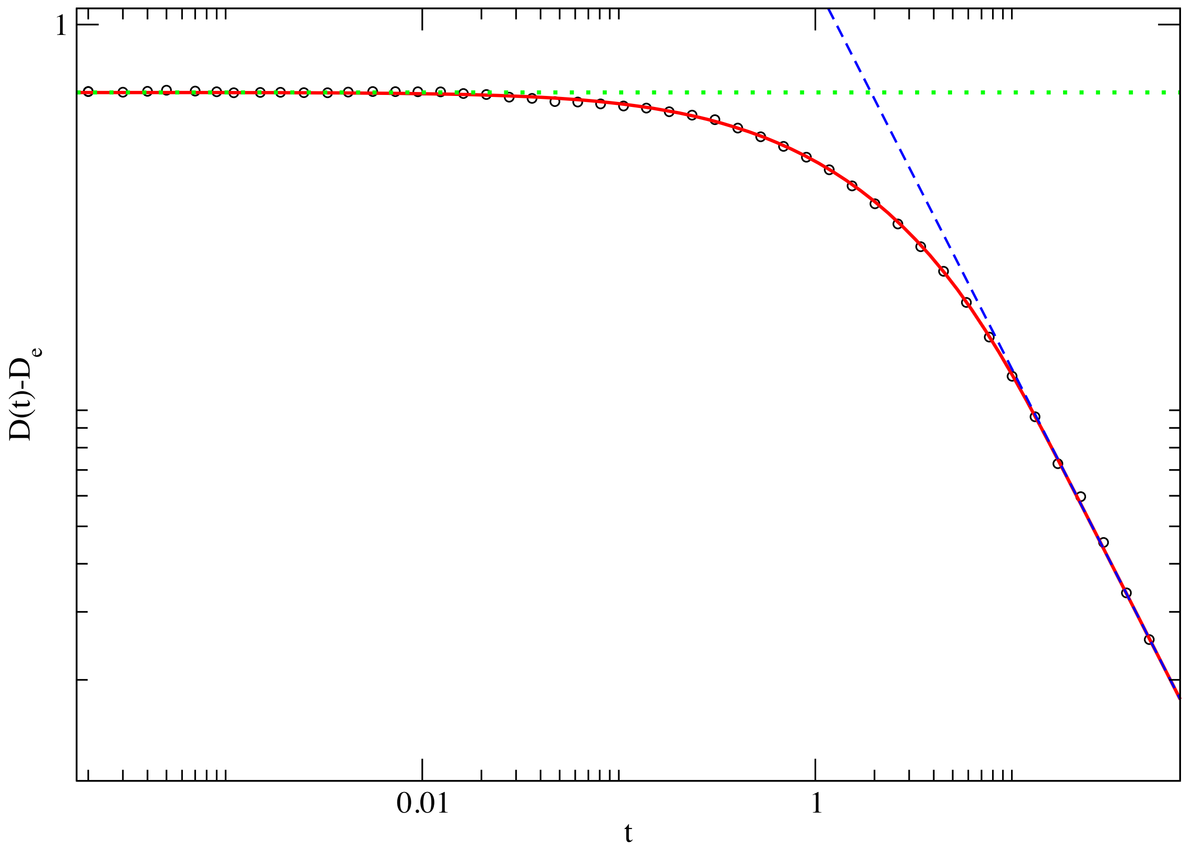
Late time asymptotics

Numerical test of full Kubo formula

$$\kappa(x) = \frac{\kappa_0}{1 + \alpha \cos(\frac{2\pi x}{l})}$$

$$l = 4\pi$$

$$\alpha = 0.8$$



Computing D_e and C

$$D_e = \overline{\kappa} - \frac{1}{d\Omega} \int_\Omega d\mathbf{x} \nabla \kappa(\mathbf{x}) \cdot \mathbf{f}(\mathbf{x})$$

$$C = \frac{1}{d|\Omega|} \int_\Omega d\mathbf{x}\ \mathbf{f}^2(\mathbf{x})$$

always postive

where
$$\mathbf{f}(\mathbf{x}) = \int_\Omega d\mathbf{y} H'^{-1}(\mathbf{x}, \mathbf{y}) \nabla \kappa(\mathbf{y})$$

Boundary conditions on **f**

(i) Periodic on Ω

(ii) $\int_\Omega d\mathbf{x}\ \mathbf{f}(\mathbf{x}) = \mathbf{0}$

Explicit results in 1d

$$f(x) = -x + A + B\int_0^x \frac{dy}{\kappa(y)}$$

Periodicity in l gives: $B = \overline{\kappa^{-1}}^{-1}$

Orthogonality to constant gives:

$$A = \frac{1}{l}\int_0^l dx \left[x - \overline{\kappa^{-1}}^{-1}\int_0^x dy\ \kappa^{-1}(y)\right]$$

Defining $\qquad r(x) = -x + \overline{\kappa^{-1}}^{-1}\int_0^x dy\ \kappa^{-1}(y)$

$$C = \frac{1}{l}\int_0^l dx\ (r(x) - \overline{r})^2$$

What we find

$$D_e = \overline{\kappa^{-1}}^{-1}$$

Recover the classic results from a dynamical Calculation !

Scaling: write

$$\kappa(x) = K(\frac{2\pi x}{l})$$

$$R(z) = -y + \frac{1}{\overline{K^{-1}}} \int_0^y dy' \; K^{-1}(y')$$

$$C = \frac{l^2}{(2\pi)^3} \int_0^{2\pi} dz \left(R(z) - \overline{R}\right)^2$$

Must have this scaling by dimensional analysis – independent of κ_0 overall scale of diffusivity

Diffusion in periodic potentials

Fokker Planck equation $$\frac{\partial}{\partial t}p(\mathbf{x},t) = \kappa\nabla\cdot\left(\nabla p(\mathbf{x},t) + \beta p(\mathbf{x},t)\nabla\phi(\mathbf{x})\right)$$

Can find a Kubo formula as before

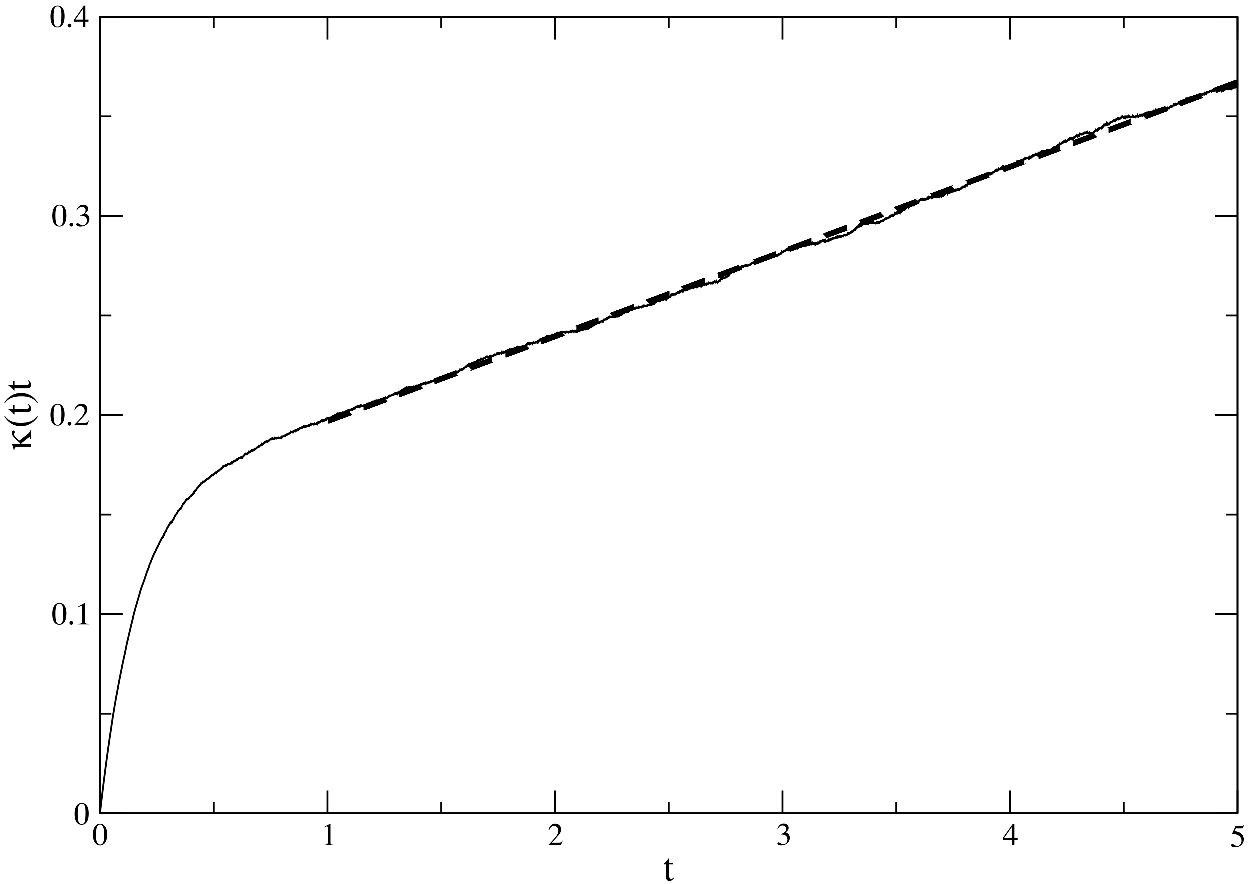
In one dimension $$\kappa_e = \frac{\kappa}{\overline{\exp(\beta\phi)}\;\overline{\exp(-\beta\phi)}}$$

S. Lifson and J. L. Jackson, J. Chem. Phys. **36**, 2410 (1962); P.G. de Gennes, J. Stat. Phys. **12** 463 (1975); R. Zwanzig, Proc. Nat. Acad. Sci. **85** 2029 (1988).

Version for discrete random walks – Derrida J. Stat. Phys. **31**, 433 (1983)

Remarkable result – again only depends on one point function but also independent of the sign of ϕ !

Numerical MSD in 1d



$$\kappa(t) = D(t)$$

FIG. 1: $\kappa(t)t$ estimated from the MSD in a numerical simulation of 10^5 Langevin particles in the potential in Eq. (67) given by $V(x) = \cos(x)$, $\beta = 3$ and $l = 4.0$ (continuous) black line. Shown as thick dashed line is the linear fit of $\kappa(t)t$ for $t > 1$ yielding the estimate $\kappa_e = 0.04258$ and $C = 0.15432$. The analytical predictions are $\kappa_e = 0.04198$ and $C = 0.15778$.

C for a periodic potential in 1d

Gibbs Boltzmann measure on cell

$$\langle A(x)\rangle_{eq} = \frac{\int_0^L dx \;\; \exp\left(-\beta\phi(x)\right) A(x)}{L\langle \exp(-\beta\phi)\rangle},$$

$$R(x) = L\left(\frac{x}{L} - \frac{1}{L\langle \exp(\beta\phi)\rangle}\int_0^x dx' \;\; \exp\left(\beta\phi(x')\right)\right)$$

$$C = \langle R^2(x)\rangle_{eq} - \langle R(x)\rangle_{eq}^2$$

again positive

Define $\phi(x) = V(\frac{2\pi x}{l})$

$$\langle R^2(x)\rangle_{eq} = \frac{l^2}{(2\pi)^2\int_0^{2\pi} dz' \exp\left(-\beta V(z')\right)}\int_0^{2\pi} dz \;\; \exp\left(-\beta V(z)\right)\left[z - \frac{\int_0^z dz' \exp\left(\beta V(z')\right)}{\frac{1}{2\pi}\int_0^{2\pi} dz' \exp\left(\beta V(z')\right)}\right]^2.$$

$$\langle R(x)\rangle_{eq} = \frac{l}{(2\pi)\int_0^{2\pi} dz' \exp\left(-\beta V(z')\right)}\int_0^{2\pi} dz \;\; \exp\left(-\beta V(z)\right)\left[z - \frac{\int_0^z dz' \exp\left(\beta V(z')\right)}{\frac{1}{2\pi}\int_0^{2\pi} dz' \exp\left(\beta V(z')\right)}\right]$$

$$C = cl^2$$

c independent of l and κ_0

Low temperature limit

Kramers' Law $$\kappa_e = \kappa 2\pi\beta\sqrt{|V''(z_{\max})|V''(z_{\min})}\exp\left(-\beta(V(z_{\max}) - V(z_{\min})\right)$$

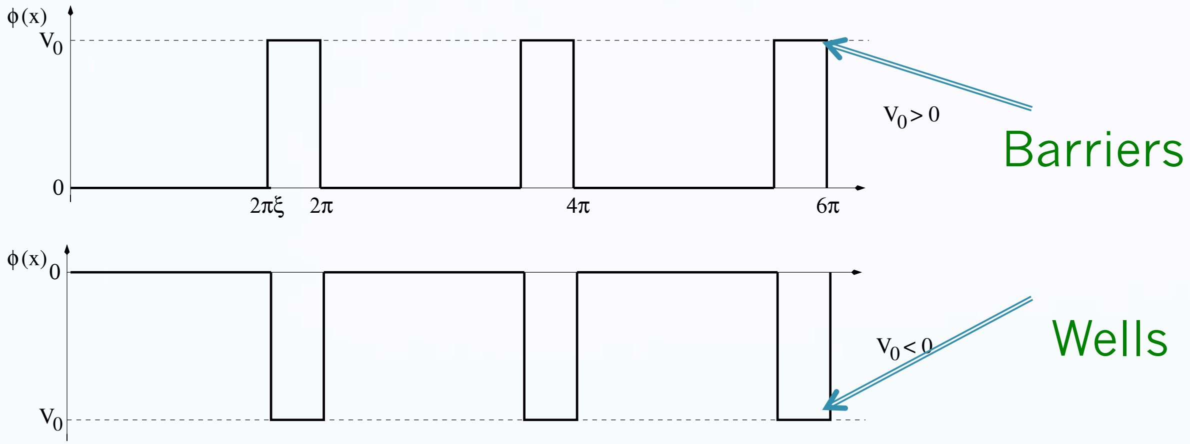
Point where maximum attained

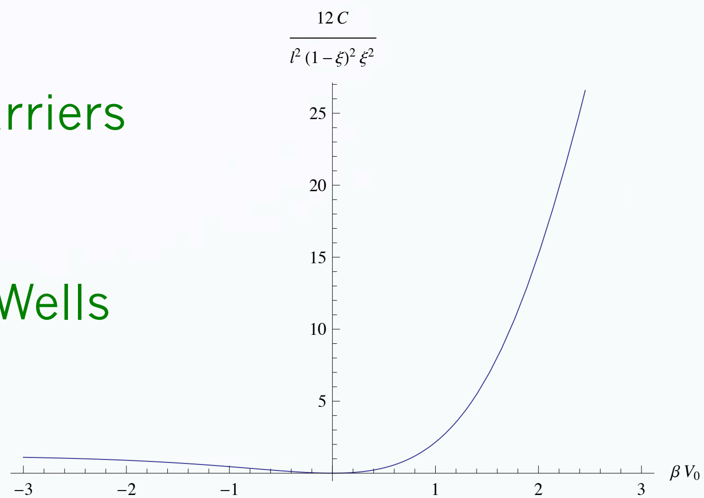
Point where minumum attained

$$C = \frac{l^2}{(2\pi)^2\beta V''(z_{\min})}$$

- so C is more sensitive to minimum of potential !

Square well potentials





$$\kappa_e = \frac{\kappa l^2}{(2\pi)^2 \left(\xi^2 + (1-\xi)^2 + 2\xi(1-\xi)\cosh(\beta V_0)\right)}$$

$$C = \frac{\xi^2(1-\xi)^2 l^2}{12}\left(\frac{\exp(\beta V_0) - 1}{\xi + (1-\xi)\exp(\beta V_0)}\right)^2$$

Conclusions

- Can derive Kubo type formula to dynamically derive effective late time diffusion constants showing equivalence between static and dynamic methods

- Late time correction in periodic systems behaves as C/t

- C depends on the spatial structure of the potential or diffusivity fields – even when κ_e depends on a one point function (in one dimension).

- Could help to interpret single particle tracking experiments and distinguish between normal and anomalous diffusion.