NANYANG TECHNOLOGICAL UNIVERSITY

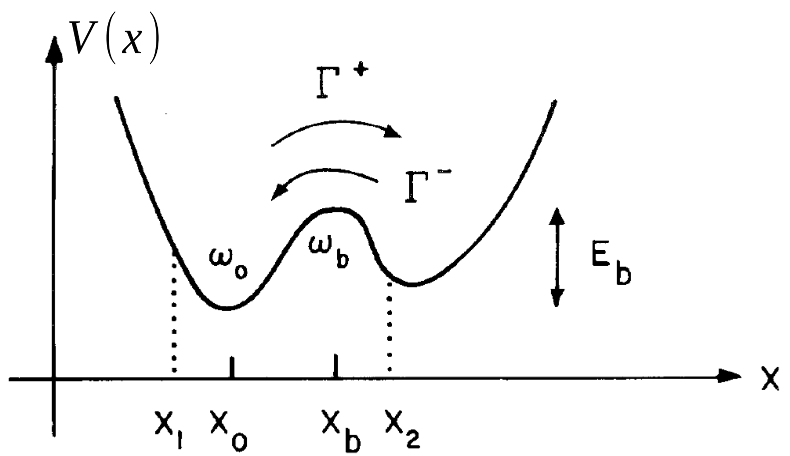
A Boltzmann transport approach to escape and diffusion problems

Antonio Piscitelli
Senior Research Fellow
Nanyang Technological University

Massimo Pica Ciamarra, Associate Professor
Roberto Arevalo, Senior Research Fellow
Cakir Abdullah, Senior Research Fellow

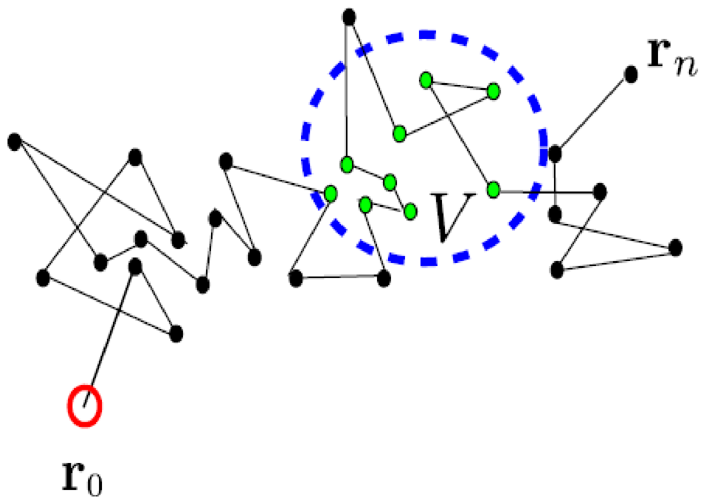
Two types of diffusion problems

Klein-Kramers equation



- In contact with a thermal bath
- Negligible timescale of interaction
- Rate of crossing a barrier

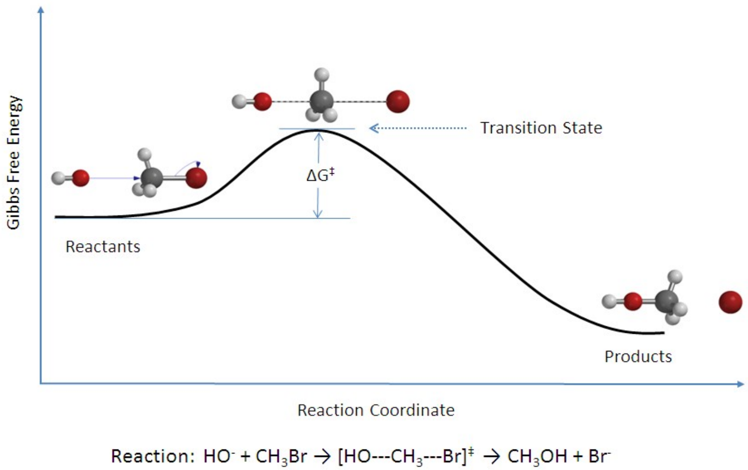
Boltzmann transport equation



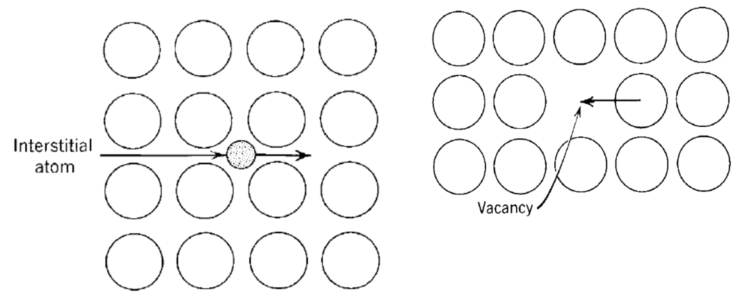
- Collisions between particles
- Finite timescale of interaction
- Most often with U(x)=0

Klein-Kramer Equation: some applications

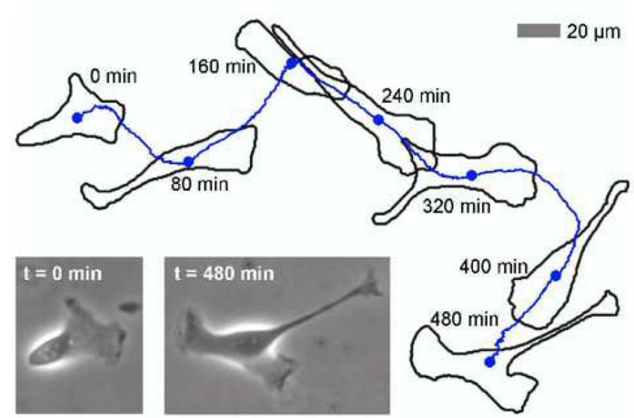
Chemical kinetics



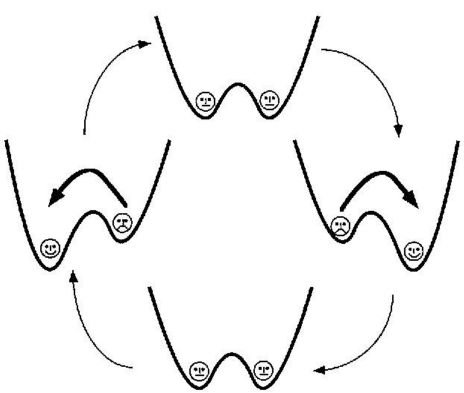
Diffusion in solids, periodic U(x)



Transport in biomolecules



Stochastic Resonance



Dielectric loss spectra of molecular liquids and solids

Current-Voltage characteristic of Josephson junctions

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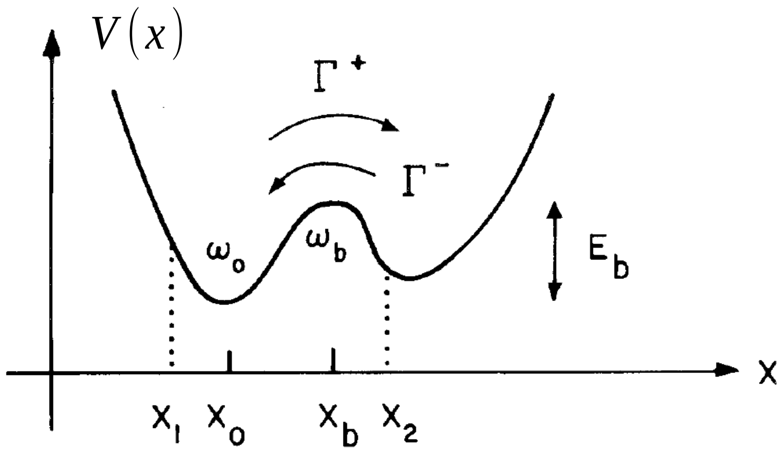
Klein-Kramer Equation: main features

$$\frac{\partial P(x,v,t)}{\partial t} = -v\frac{\partial P}{\partial x} + \frac{1}{m}\frac{\partial V(x)}{\partial x}\frac{\partial P}{\partial v} + \gamma\frac{\partial (vP)}{\partial v} + \frac{\gamma k_B T}{m}\frac{\partial^2 P}{\partial v^2}$$

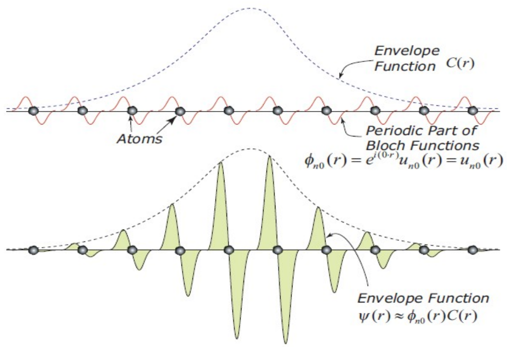


$$\Gamma^+ = \left(\frac{\mu(\gamma,\omega_b)}{\omega_b}\frac{\omega_0}{2\pi}\right)e^{-\frac{E_b}{k_B T}}$$

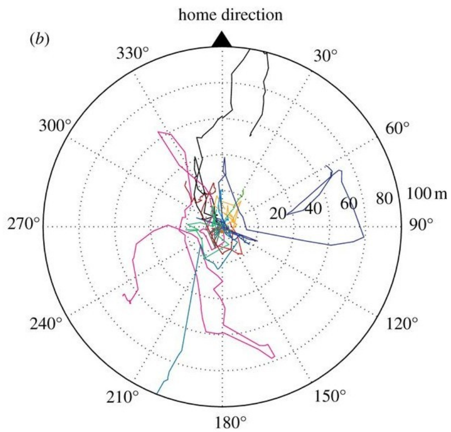
- Boltzmann equilibrium as stationary state
- Equilibrium achieved through dissipation: Fluctuation – Dissipation theorem
- Escape rate: perturbation of equilibrium near the top of the barrier
- Escape rate: geometric prefactor and Arrhenius temperature dependence

Boltzmann Transport Equation: some applications

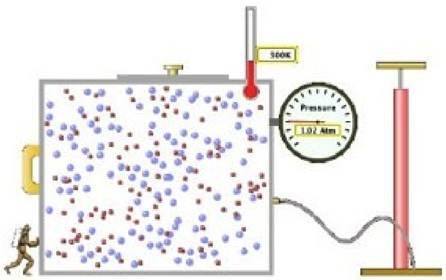
-ELECTRONICS
Electron Transport in Semiconductors



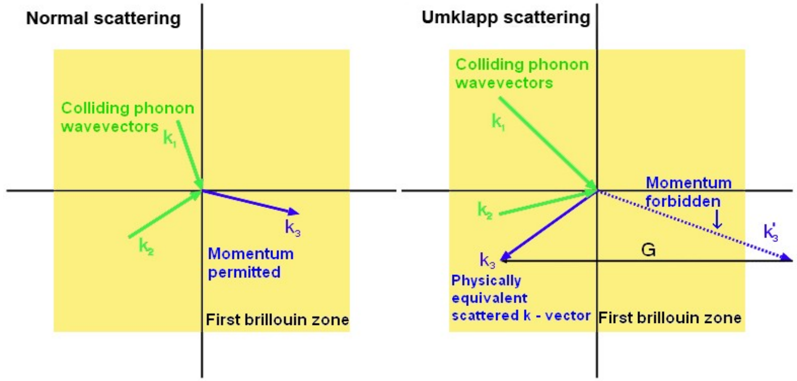
- BIOLOGY
Research strategies



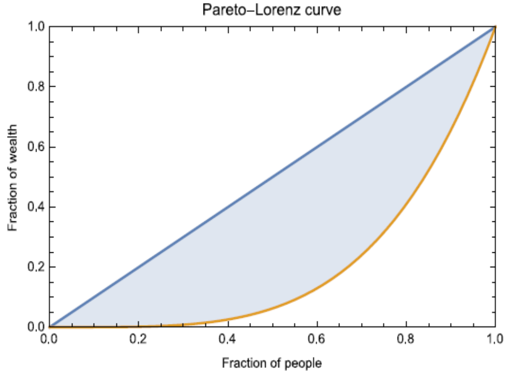
- GAS DYNAMICS



- SOLID STATE
Anharmonicity in crystalline solids
(thermal conducibility)



- ECONOMY
Agent-based asset exchange models



Boltzmann Transport Equation: Relaxation Time Approximation

Boltzmann equation

Collision integral

$$\frac{\partial f}{\partial t} + \vec{v} \cdot \vec{\nabla}_{\vec{r}} f + \vec{F} \cdot \nabla_{\vec{k}} f = \left(\frac{\partial f}{\partial t} \right)_c$$

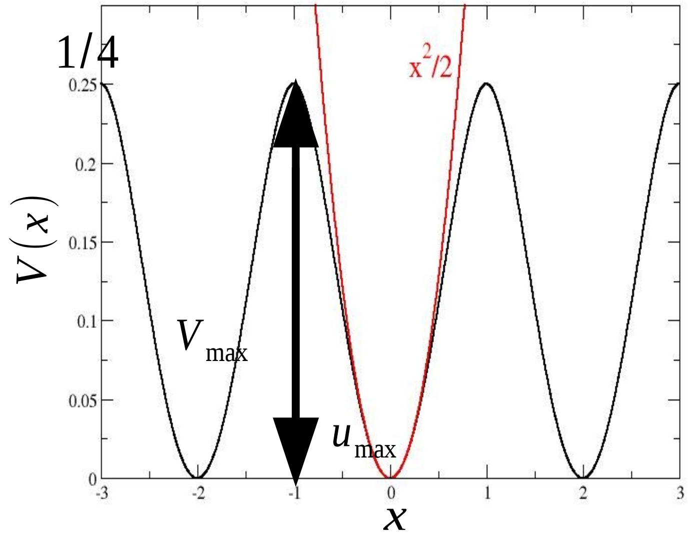
Perturbation of a free Hamiltonian $\longrightarrow$ Interaction

In principle: Cross sections of all possible processes from Fermi golden - rule

In practice: - Exponential approach to equilibrium: $\left(\frac{\partial f_i}{\partial t} \right)_c = \frac{f_i - f_{0,i}(T, E)}{\tau_i(\vec{k})}$

- Exponential prob of time distribution of the interaction

The model: Collisions in the standard well



$$V_{max} = 1/4 \qquad u_{max} = 1$$

$$V(x) = \frac{1}{2}x^2 - \frac{1}{4}x^4 \qquad v_x = \sqrt{2(E - V(x))}$$

$$\ddot{x} = -x + x^3 + \eta_{\mathrm{scatt}}(t_c)$$

$\eta_{\mathrm{scatt}}(t_c)$: we randomize velocity every Δt from $P(\Delta t) \sim \exp(-\Delta t / t_c)$

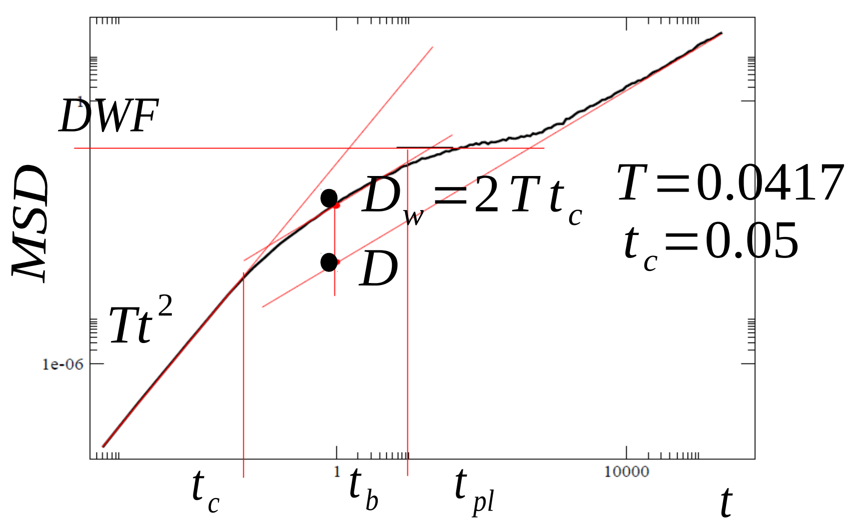
$$\begin{cases} \dot{x} = \begin{cases} v \text{ if } t \neq \Delta t \\ w \text{ if } t = \Delta t, w \text{ random from } P(w) \end{cases} \\ \dot{v} = -\dfrac{\partial V}{\partial x} \end{cases} \qquad P(w) \sim \frac{\exp(-w^2/2T)}{\sqrt{2\pi T}}$$

Boltzmann distribution is conserved at all the times:

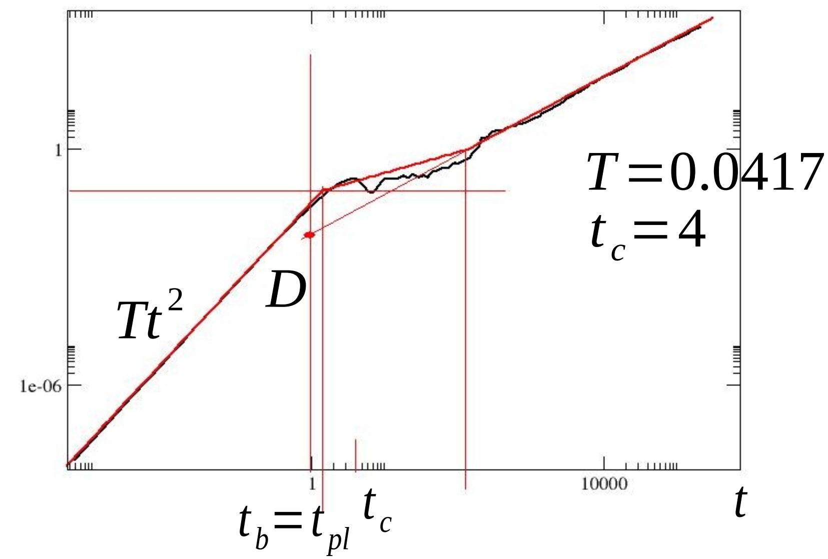
- Between collisions: it solves Liouville's equation
- At collisions: the reshuffle preserves it

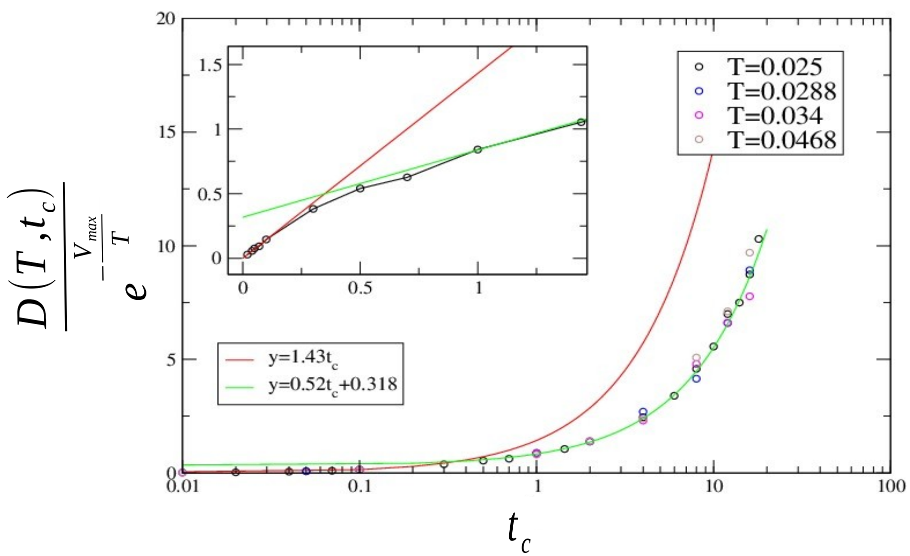
Finite collision time ranges

$t_c < t_b(T)$



$t_c > t_b(T)$





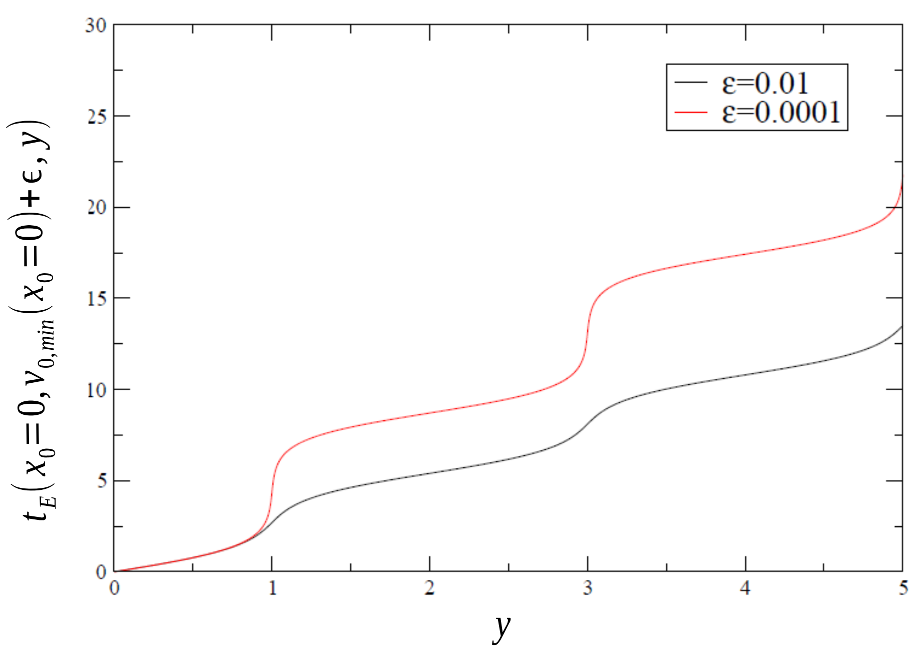
Integral expression for diffusion

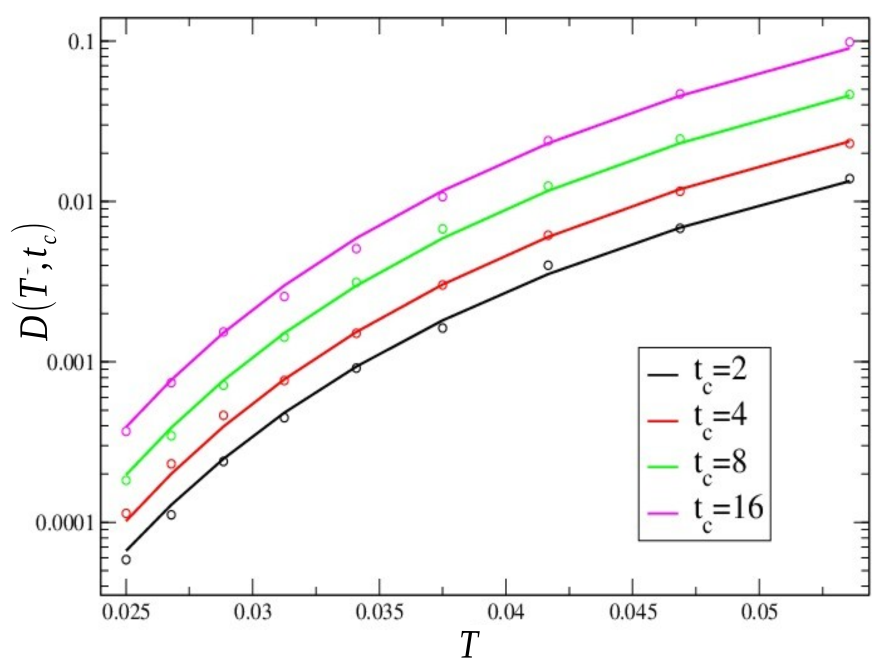
$$D=\frac{\langle(\Delta x)^2\rangle}{t_c}=2\int_{-1}^{1}dx_0\int_{v_{0,min}(x_0)}^{\infty}dv_0\int_{1}^{\infty}dy\, f_{T,t_c}(x_0,v_0,y)$$

$\langle\ldots\rangle$ = Average over the jumps (starting from equilibrium)

$$f_{T,t_c}(x_0,v_0,y)\propto P_{Boltz}(x_0,v_0)\,\frac{e^{-\frac{t_E(x_0\rightarrow y)}{t_c}}}{v_y}\,\frac{(y-x_0)^2}{t_c}$$

= Contribution of the jump (x_0, v_0, y) to the diffusion



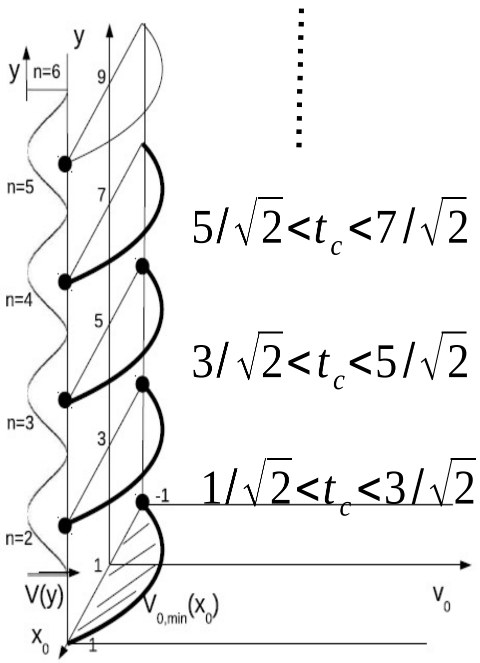


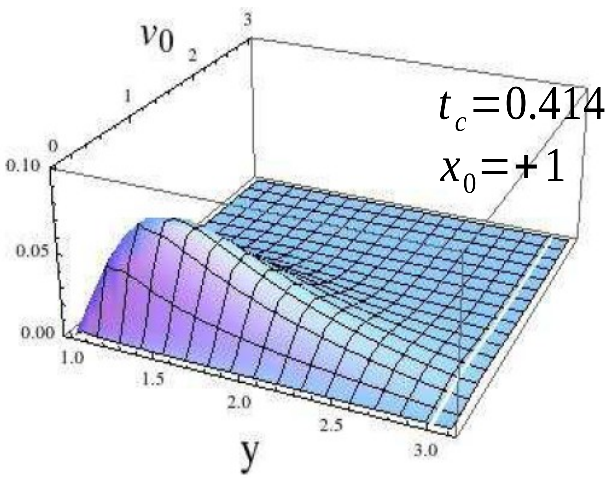
Important jumps

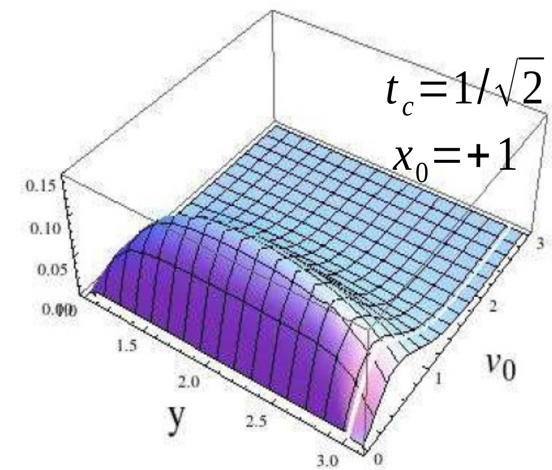
There are no internal maxima, but

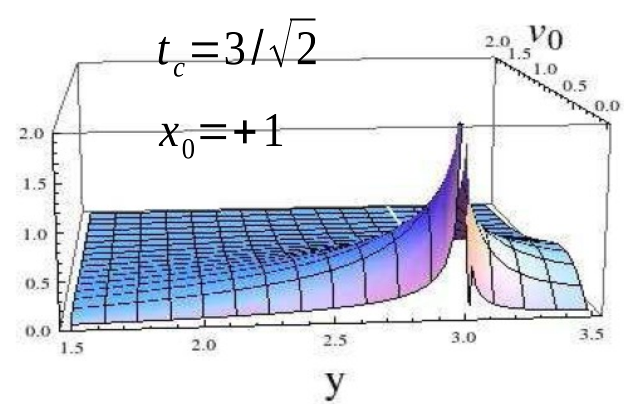
$$\lim_{y\to 1^+} f(x_0, v_0, y) = \begin{cases} +\infty, t_c > \frac{1}{\sqrt{2}} \\ 0, t_c = \frac{1}{\sqrt{2}} \\ -\infty, t_c < \frac{1}{\sqrt{2}} \end{cases}$$

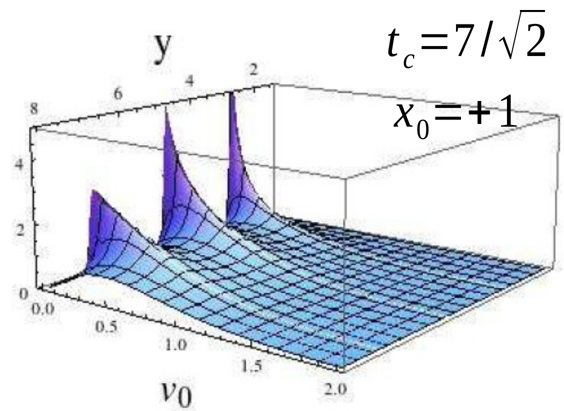
$$-1 < x_0 < 1$$



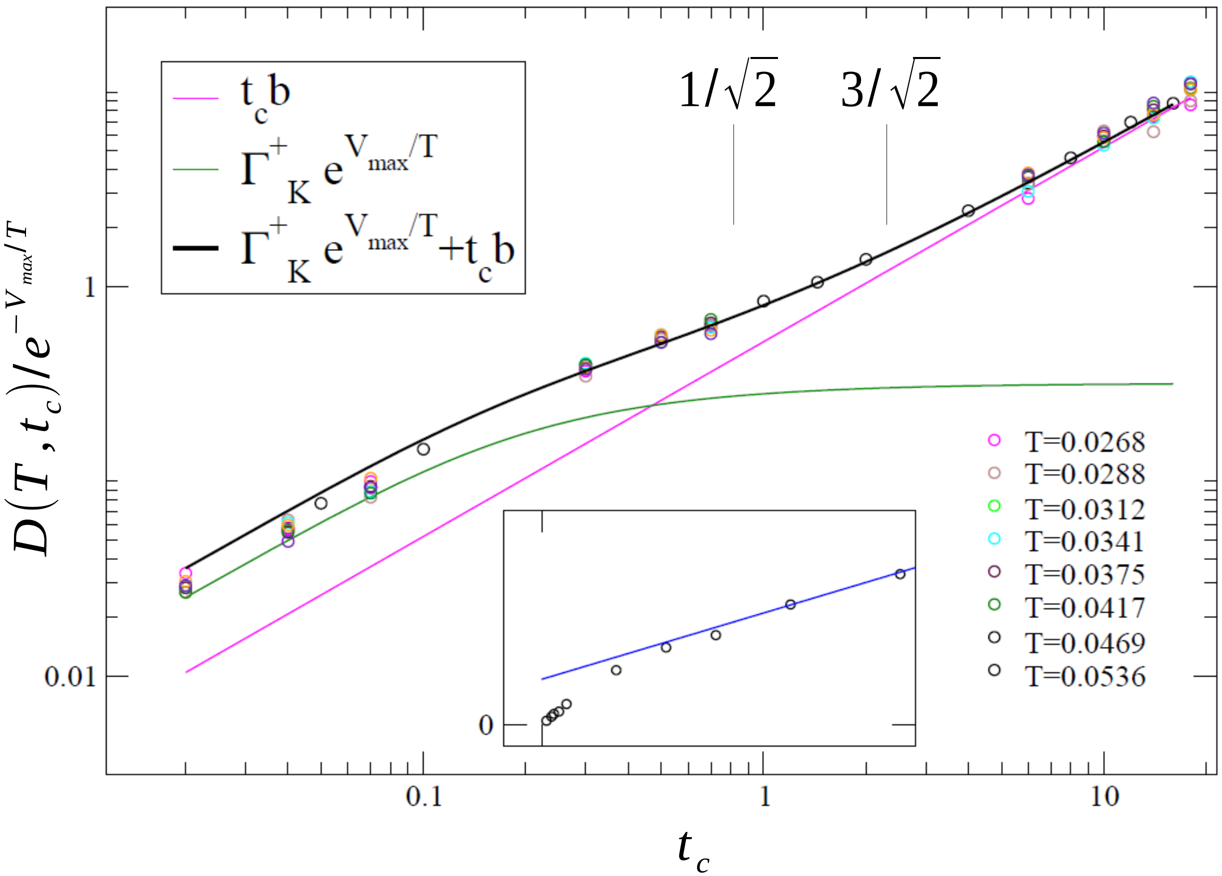








Low temperature mastercurve



$$D(T,t_c) =$$

$$\Gamma^+(T,\gamma=1/2\,t_c) + b\,t_c\,e^{-V_{max}/T}$$

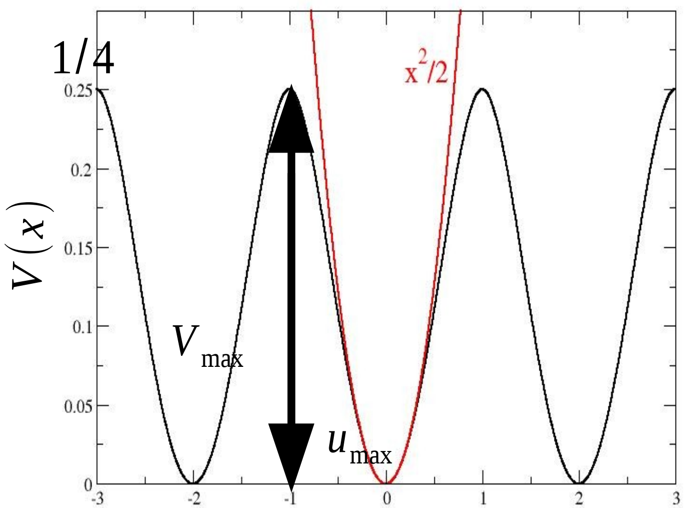
for t_c *above crossover*

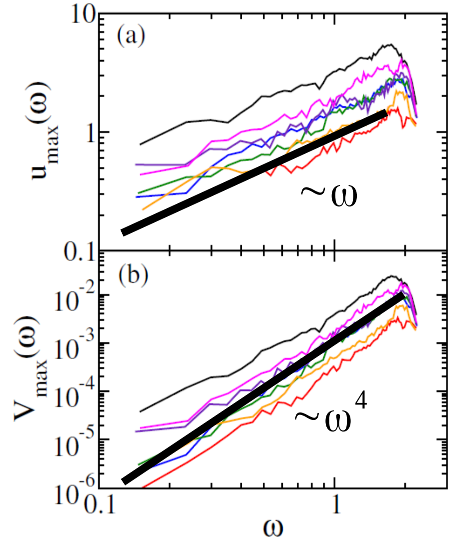
$$\frac{D(T,t_c)}{e^{-\frac{V_{max}}{T}}} = a + b\,t_c$$

$$a = \lim_{\gamma\to 0} \frac{2\Gamma^+}{e^{-\frac{V_{max}}{T}}} = \frac{1}{\pi} \sim 0.318$$

$$b \sim 0.52$$

Energy landscape of harmonic spheres



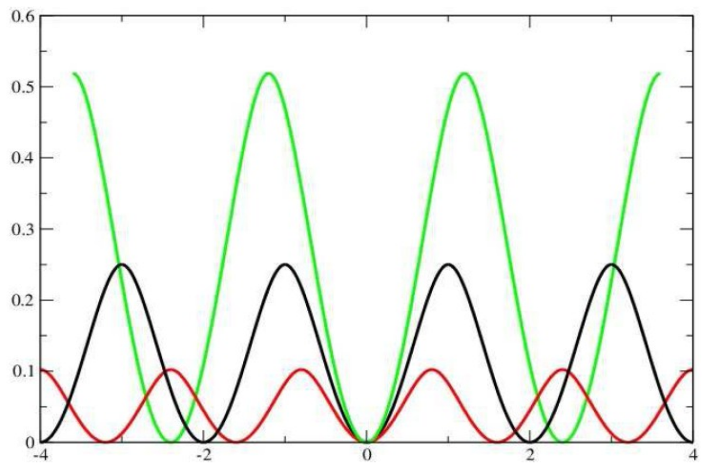


$$V_\omega(x)=\frac{1}{2}m\omega^2x^2-\frac{1}{4}Bx^4$$

$$u_{\max}=\omega\sqrt{\frac{m}{B}}$$

$$V_{\max}=\frac{m^2\omega^4}{4B}=\frac{u_{\max}^4 B}{4}$$

$V_{max}(\omega)$

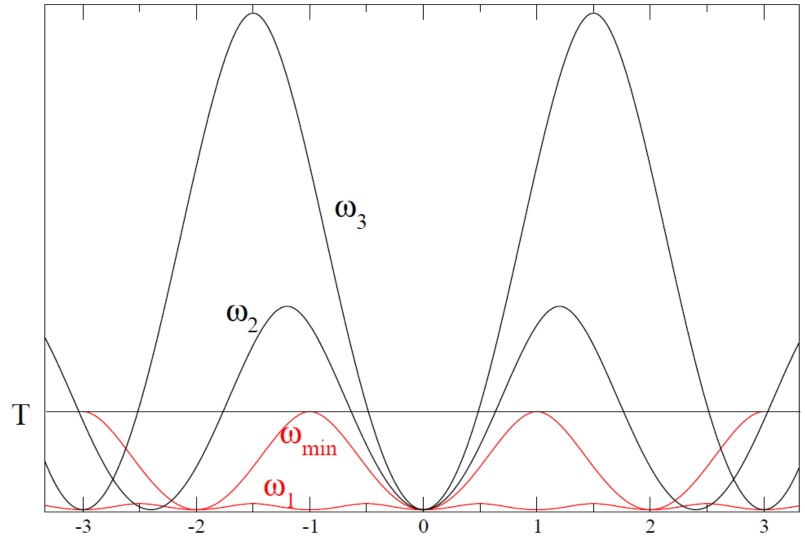


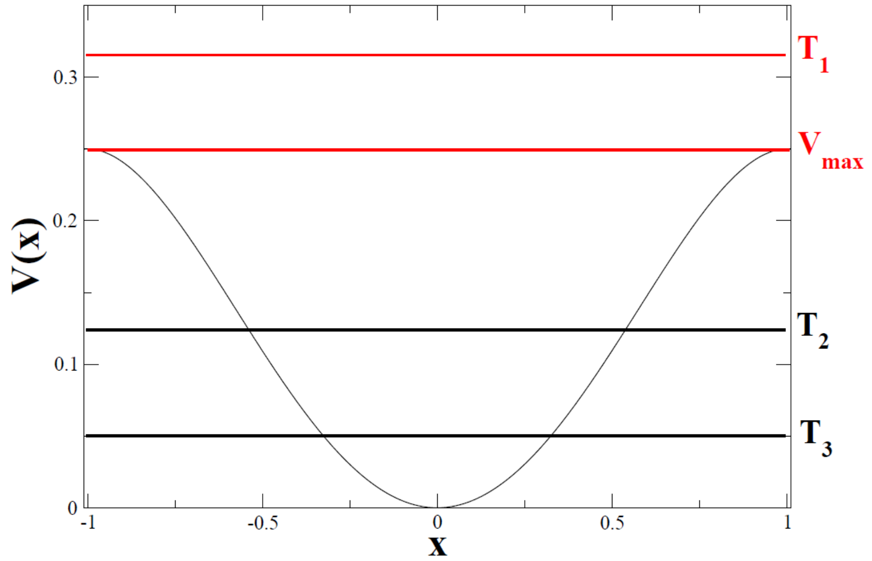
Adimensional equations: one ω for all

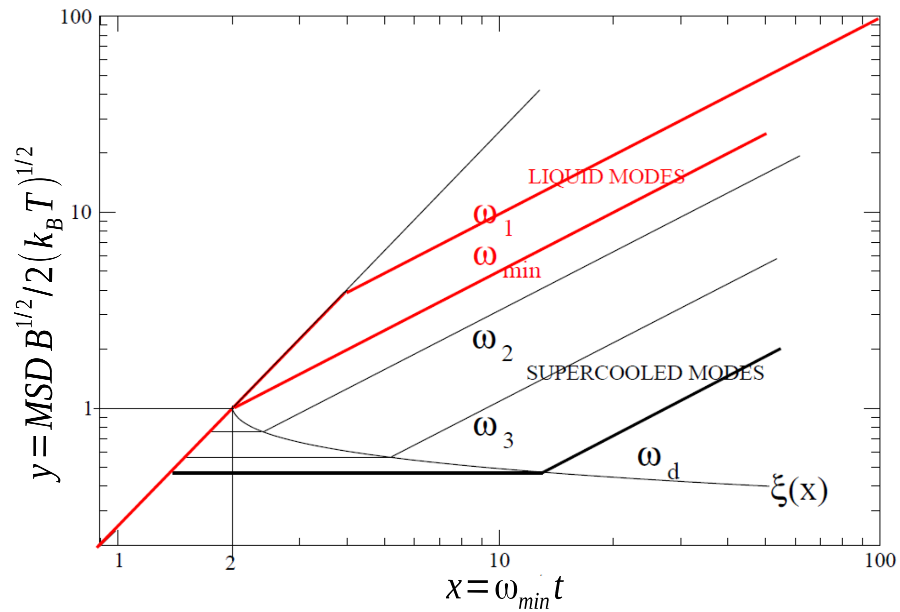
$$\boldsymbol{T}=\frac{T}{4V_{\max}}=\frac{TB}{m^2\omega^4} \qquad \boldsymbol{X}=\frac{x}{\sqrt{m\omega^2/B}}$$

$$\boldsymbol{t}=t\omega \qquad \boldsymbol{V}_{\boldsymbol{max}}=1/4 \qquad \boldsymbol{u}_{\boldsymbol{max}}=1$$

Single modes and sum over the modes







$$D(T) = \int D^{(liq)}(\omega)\, d\omega + \int D^{(s)}(\omega)\, d\omega = \ldots$$

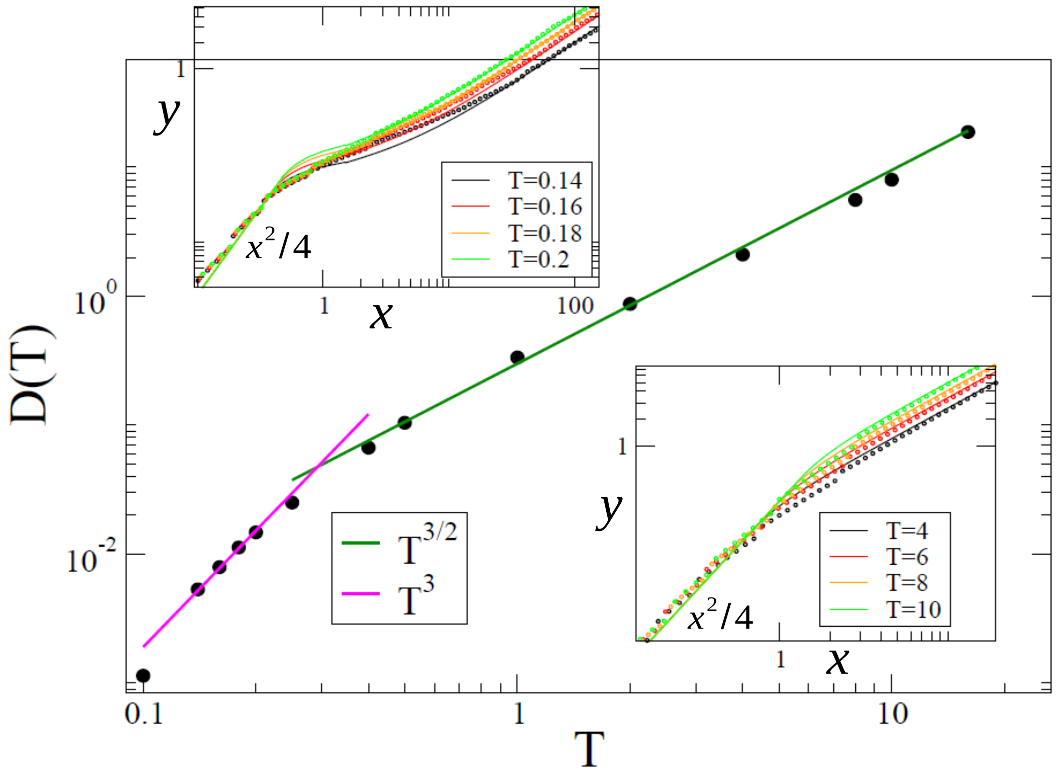
$$= \frac{3(k_B T)^{3/2} B^{1/2}}{\omega_d^{\,3}(T) M^2}\left(4 + 8aK_2^{(a)} + 16bK_2^{(b)}\right)$$

$$\propto 65\%(\mathit{Liquid\ modes}) +$$

$$+ 26\%(\mathit{From\ inside\ the\ well\ jumps})$$

$$+ 9\%(\mathit{Kramer-like\ jumps})$$

Sum over the modes:
Harmonic Spheres Diffusion Constant



$$t_c = t_b(T)$$

Debye DoS

$$d(\omega) = \begin{cases} 3\dfrac{\omega^2}{\omega_d^3} & \omega \leqslant \omega_d \\ 0 & \omega > \omega_d \end{cases}$$

$$\omega_d \sim const / t_b^{(harm)}(T) \sim 1/\sqrt{T}$$

Low temperatures (supercooled regime)

$$D(T) \propto \frac{(k_B T)^3 B^{1/2}}{M^2}$$

High temperatures (liquid regime)

$$D(T) \propto \frac{(k_B T)^{3/2}}{M}$$

Summary

Numerical study of a particle in a periodic well potential

What if: finite intercollision time and
non-dissipative dynamics
(instead of BM)

CROSSOVER in t_c:
of $D(T, t_c)$ at low T

- Kramer-like → Jumps from the top of the barrier
- Linear term → Jumps from inside the well

Consequences of:

- $t_c = t_b(T)$
- $V_{max}(\omega) \propto \omega^4, \quad u_{max}(\omega) \propto \omega$
- $Debye\ DoS$
- $D(T) = \int D_\omega(T)\, d\omega$

- There is ω_{min} such that $T > V_{max}(\omega)$ for all $\omega < \omega_{min}$
These are the “liquid” modes
- Relative contributions to $D(T)$ of 1)Kramer-like 2)Linear 3)Liquid modes terms are independent of all the parameters
- $D(T) \propto T^\alpha$ and there is a crossover in α, increasing the temperature, when the last mode ω_d becomes liquid