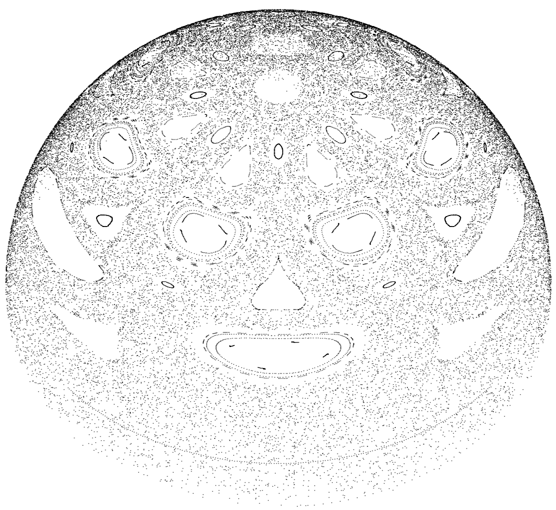
Motion through an oscillator chain: diffusion and linear response

S. De Bièvre (Université de Lille)

“Numerical methods in molecular simulation”



Bonn– Hausdorff Institute for Mathematics

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Introduction

THE SETTING Hamiltonian models of quantum or classical particles in contact with an environment having a very large number of degrees of freedom have been used to address a great variety of questions:

Proofs of return to thermal equilibrium; Derivations of a reduced dynamics for the particle: (generalized) Langevin, Fokker-Planck or Master equations; Conditions for normal or anomalous diffusion; Microscopic models for dissipation and friction ; Derivations of Ohm's law (linear response theory) or other macroscopic laws; Attempts to compute transport coefficients from microscopic dynamics . . .

A subclass of models deals with the case where the particles interact with vibrational (or harmonic) degrees of freedom of the environment. This will be the case in this talk. I will study the motion of a free particle driven by an external field F through a periodic array of monochromatic oscillators in thermal equilibrium at positive temperature.

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WHY?

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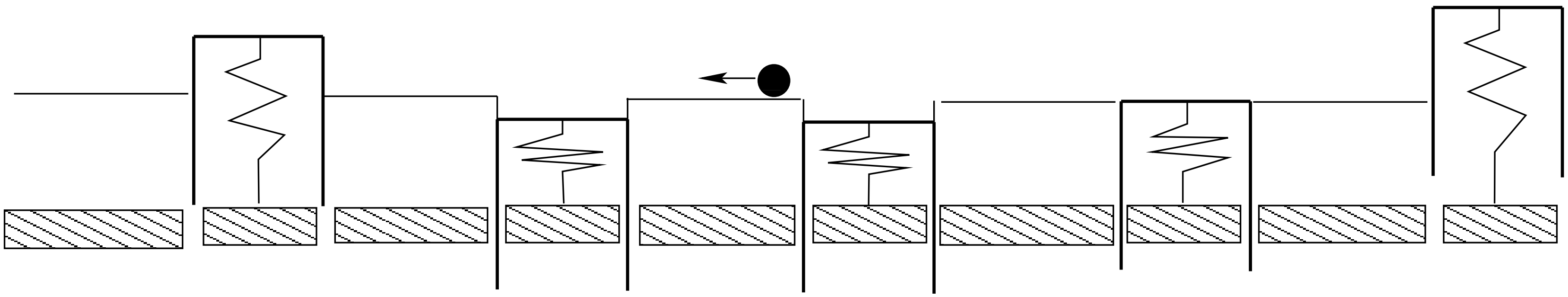
WHY? Find a Hamiltonian model in which Ohm's law holds and prove it does!

THE MODEL : a classical Holstein molecular crystal model

or

A 1-d inelastic Lorentz gas

.B., P. Parris and A. Silvius (Missouri), Physica D, **208**, 96-114 (2005); Phys. Rev. B 73, 014304 (2006)



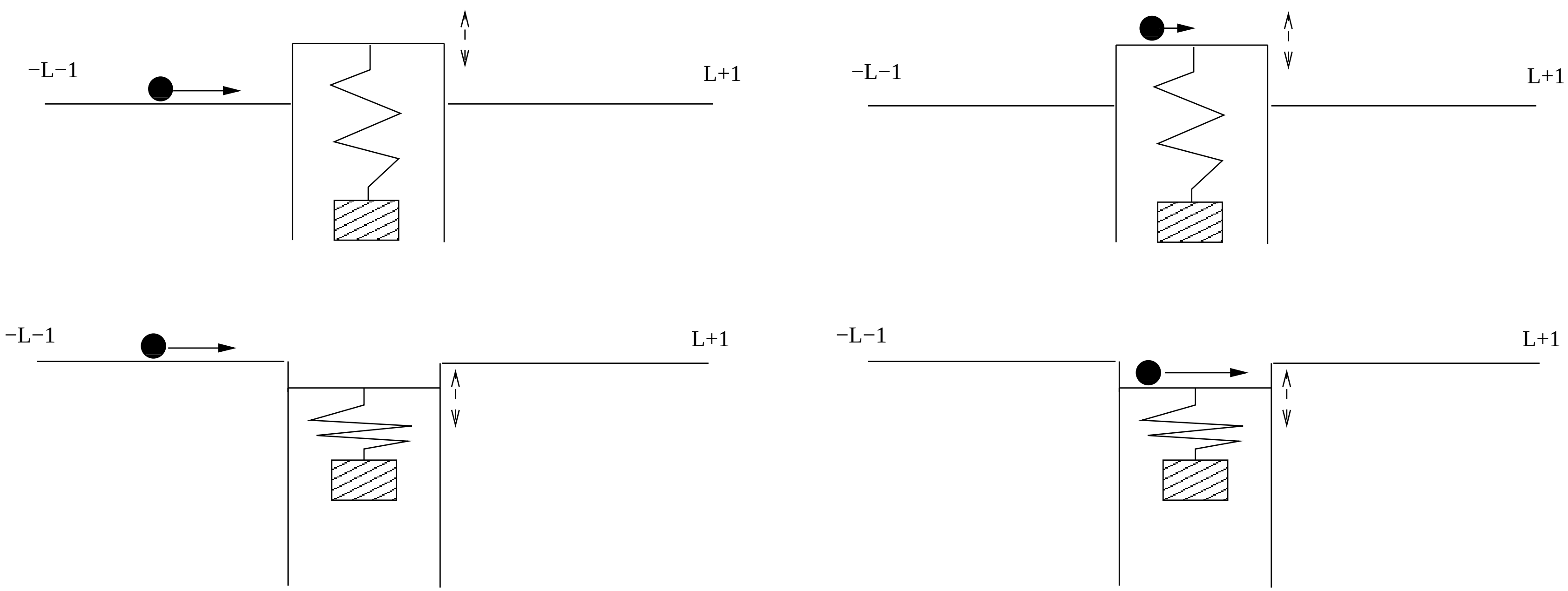
A one-dimensional periodic array (with period a) of identical oscillators of frequency ω. The particle interacts with the oscillator at ma if it is within a distance $\sigma < \frac{a}{2}$.

$$H = \frac{1}{2}p^2 + \sum_{m\in\mathbb{Z}} \frac{1}{2}\left(p_m^2 + \omega^2 q_m^2\right) + \alpha \sum_m q_m n_m\left(q\right) - Fq. \qquad (1)$$

where $n_m\left(q\right)$ vanishes outside the interaction region associated with the oscillator at ma and is equal to unity inside it.

THE DYNAMICS (no external field: $F = 0$)

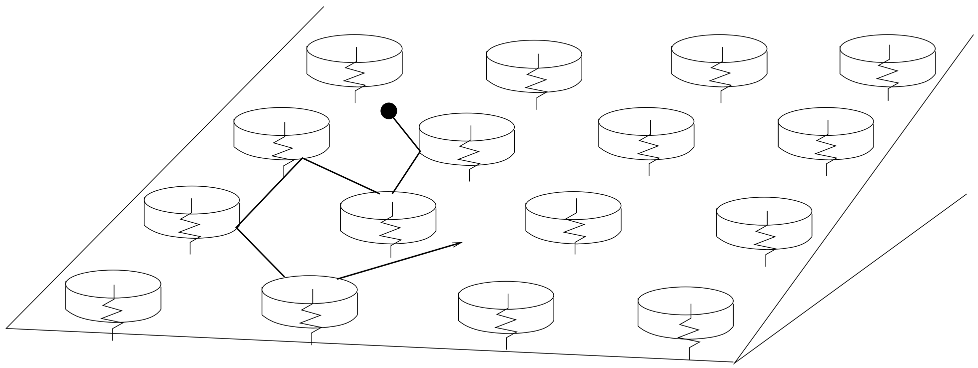
The particle moves at constant speed, except when entering or leaving the interaction region, when the oscillator displacement serves as a potential barrier: energy conservation then decides whether the particle reverses direction or not and how its speed changes. Two examples of what may happen:



If $F > 0$, the particle accelerates between collisions.

The pinball machine and Ohm's law

- The pinball machine (or the inelastic Lorentz gas)



Does the particle acquire a constant drift speed?

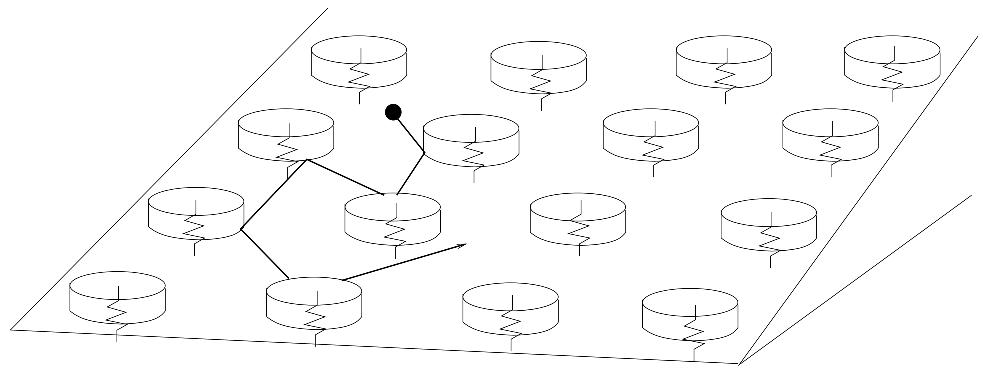
If so, how does it depend on the slope?

And on the temperature (= mean vibrational energy) of the obstacles?

Towards a Hamiltonian model for Ohm's law?

The pinball machine and Ohm's law

- The pinball machine (or the inelastic Lorentz gas)



Does the particle acquire a constant drift speed?

If so, how does it depend on the slope?

And on the temperature (= mean vibrational energy) of the obstacles?

In other words, does this provide a Hamiltonian model for Ohm's law?

- Ohm's law: $V = RI$ or $\vec{E} = \rho\vec{j}$ or $\vec{v} = \frac{\mathrm{q}\tau}{m}\vec{E}$.

$$m\frac{d\vec{v}}{dt} = \mathrm{q}\vec{E} - \frac{m}{\tau}\vec{v}, \qquad \vec{v}(t) \sim \frac{\mathrm{q}\tau}{m}\vec{E} \quad (t \to \infty).$$

THE PLAN

STEP 1 Check whether the one-dimensional classical Holstein molecular crystal model provides a Hamiltonian model for Ohm's law by computing its transport properties both when $F = 0$ and when $F > 0$ through a numerical integration of the Hamiltonian dynamics generated by

$$H = \frac{1}{2}p^2 + \sum_{|m| \leq M} \frac{1}{2}\left(p_m^2 + \omega^2 q_m^2\right) + \alpha \sum_{|m|} q_m n_m\left(q\right) - Fq. \qquad (2)$$

for suitably large M.

STEP 2 Explain the numerical results in physical terms.

STEP 3 Make conjectures, write theorems and their proofs.

REMARKS The Hamiltonian (when $F = 0$) contains only two dimensionless parameters in terms of which all relevant quantities can and must be expressed:

- E_B/E_0: here $E_B = \frac{\alpha^2}{2\omega^2}$ is the binding energy and $E_0 = \sigma^2\omega^2$.
- $2\sigma/L$: here $L = a - 2\sigma$ is the size of the non-interacting region in a cell.

In addition, all computed quantities depend on the temperature T of the system. The latter enters through the initial condition $=$ Boltzmann distribution $=$ Gibbs measure. High (low) temperature means $kT >> E_B$ ($kT << E_B$) or $\beta E_B << 1$ ($\beta E_B >> 1$) with $\beta = (kT)^{-1}$.

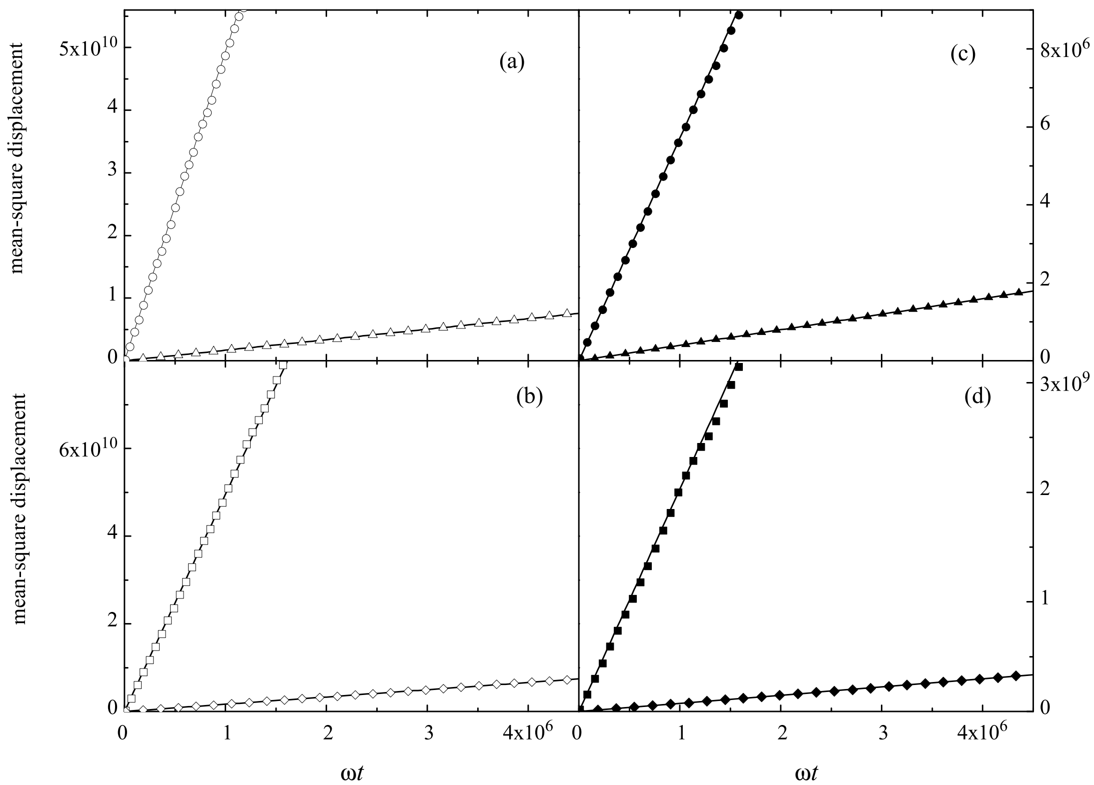
Time is measured in multiples of the oscillator period $2\pi/\omega$

When $F > 0$ there is an extra energy scale Fa. For example small F will then mean $Fa << E_B$ and $Fa\beta << 1$.

Many degrees of freedom, but only 4 parameters!

STEP 1 $F = 0$: TO DIFFUSE OR NOT TO DIFFUSE?

We injected a thermal distribution of (10^3 to 10^5) particles at inverse temperature β into an array of (5×10^4) oscillators, also in equilibrium at the same temperature. We computed $\langle q^2(t) \rangle$ (for t up to 5×10^6) and observed this:



(a) $\beta E_B = 0.015$ (c) $\beta E_B = 0.$

$\frac{E_B}{E_0} = 0.5, \frac{2\sigma}{L} = 0.5$ (triangles)

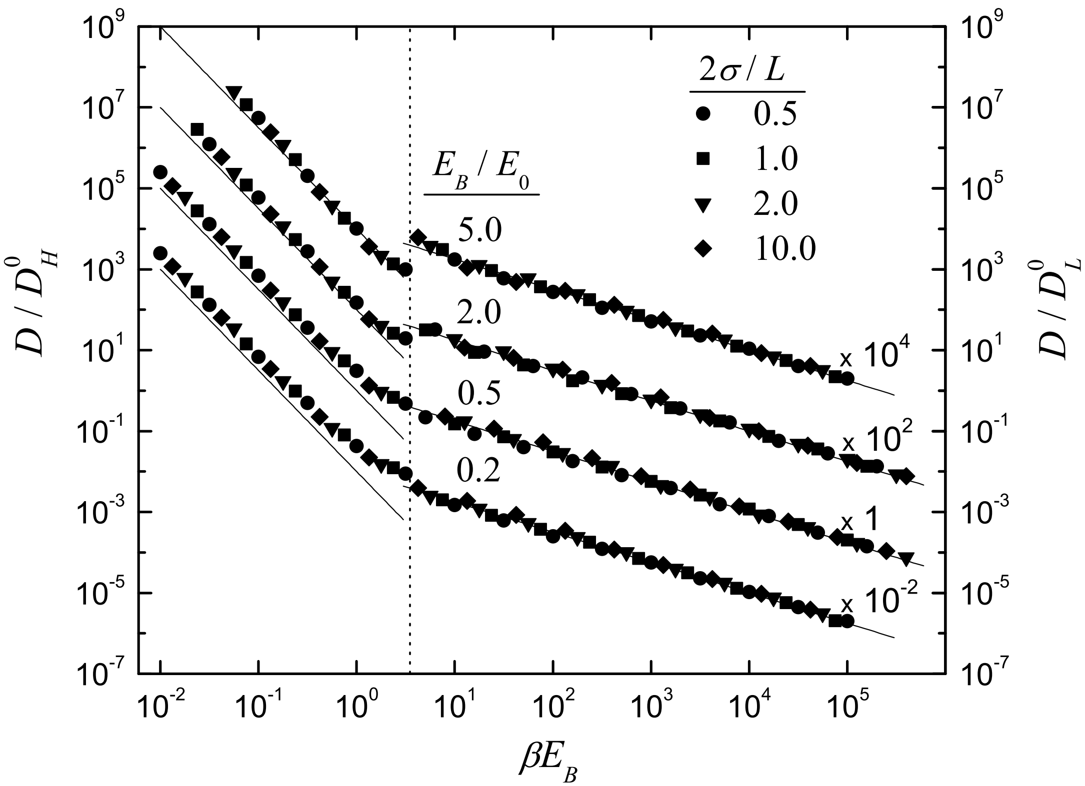
$\frac{E_B}{E_0} = 5, \frac{2\sigma}{L} = 0.5$ (cercles)

(b) $\beta E_B = 0.020$ (d) $\beta E_B = 0.$

$\frac{E_B}{E_0} = 0.5, \frac{2\sigma}{L} = 2$ (diamants)

$\frac{E_B}{E_0} = 5, \frac{2\sigma}{L} = 2$ (carrés).

Certainly, $\langle q^2(t) \rangle \sim 2Dt$. But how does D depend on $\beta E_B, E_B/E_0, 2\sigma/L$?



High temperature: $D \sim D_H^0 (\beta E_B)^{-5/2}$

$$D_H^0 = \sqrt{\frac{9 E_B a^2}{32\pi}} \frac{E_B}{E_0}$$

Low temperature: $D \sim D_L^0 (\beta E_B)^{-3/4}$

$$D_L^0 = \frac{a}{2\sigma} \Gamma(3/4) \sqrt{\frac{E_B a^2}{2\pi^2}}$$

Diffusion with a monochromatic bath!

STEP 2 $F = 0$: EXPLAINING THE POWER LAW

● At **high temperatures** Traversal time $<<<$ oscillator period and the typical potential energy barrier $\Delta \sim \sqrt{2E_B kT} <<<$ particle energy. A thermalized particle passes through many interaction regions in succession before slowing down and undergoing a velocity reversing (or randomizing) kick back up to thermal velocities: relaxation time approximation.

For fast particles the energy loss per site is: $\Delta E = -4E_B E_0/p^2$. As a result, a particle of momentum p takes an average time $\tau(p) = \frac{p^3 a}{12 E_\mathrm{B} E_0}$ to travel an average distance $\ell(p) = \frac{p^4 a}{16 E_\mathrm{B} E_0} = \frac{3}{4} p\tau(p)$. This leads to a random walk with pausing times $\tau(p)$ and steps $\ell(p)$ so that

$$D = \frac{\langle \ell^2 \rangle}{2\langle \tau \rangle} \sim (\beta E_B)^{-5/2}.$$

Adiabatic regime: the random potential seen by the particle typically changes adiabatically with respect to the particle's net motion (*cfr.* polaron).

● **Low temperatures**: Traversal time $>>>$ oscillator period.

Hopping transport.

STEP 3 $F = 0$: CONJECTURES, THEOREMS AND PROOFS

Conjecture For all, E_B, E_0 and $0 < \beta < +\infty$,

$$\lim_{t \to +\infty} \frac{\langle (q(t) - q(0))^2 \rangle}{2t} := D(\beta)$$

exists and satisfies

$$\lim_{\beta \to +\infty} (\beta E_B)^{3/2} D(\beta) := D_L > 0, \quad \lim_{\beta \to 0} (\beta E_B)^{5/2} D(\beta) := D_H > 0.$$

...

TURNING ON THE FIELD: $F > 0$

with P. Lafitte (UST Lille, CNRS, INRIA) and P. Parris (Missouri-Rolla): JSP, to appear.

QUESTION: Does the particle reach a limiting drift velocity, defined as

$$v_F := \lim_{t \to +\infty} v_F(t) := \lim_{t \to +\infty} \frac{\langle q(t, F) \rangle}{t}$$

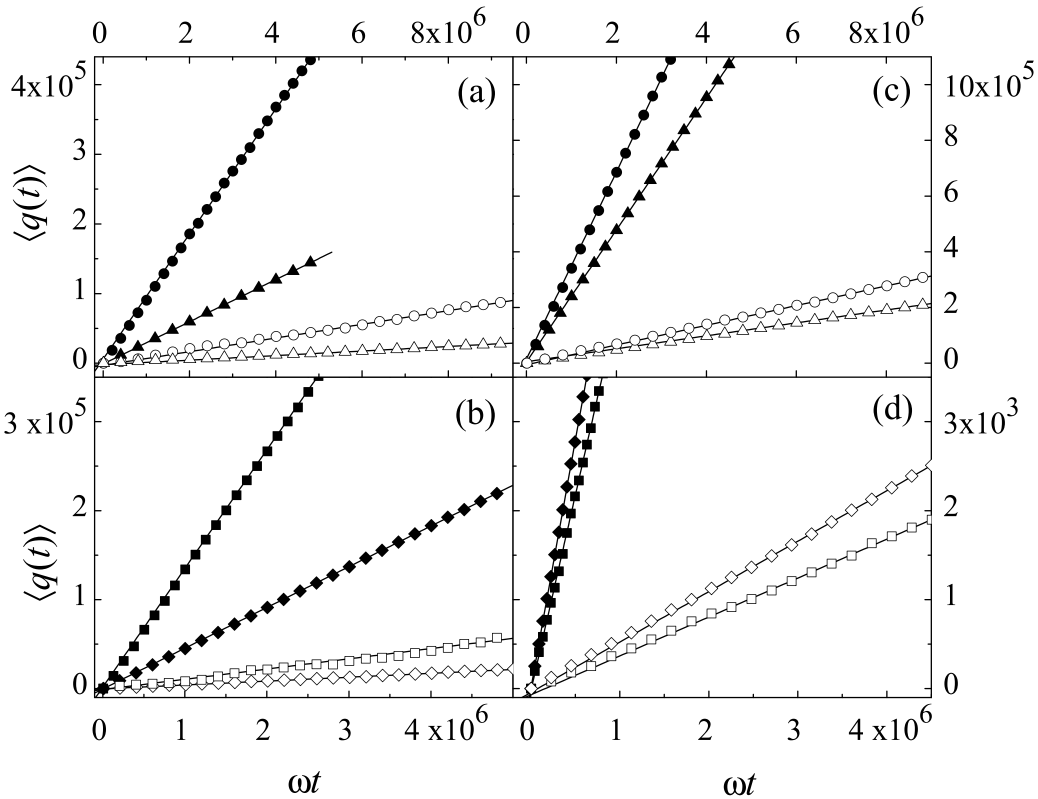
and is the latter linear in F, at least for small F?

In other words, does v_F exist and if so, does the zero field mobility μ, defined by

$$\mu := \lim_{F \to 0} \frac{v_F}{F}$$

exist? In other words, is the system Ohmic?

STEP 1 $F > 0$ To drift or not to drift?



(a) $\beta E_B = 0.015$ (c) $\beta E_B = 0.50$

$\frac{E_B}{E_0} = 0.5, \frac{2\sigma}{L} = 0.5$ (triangles)

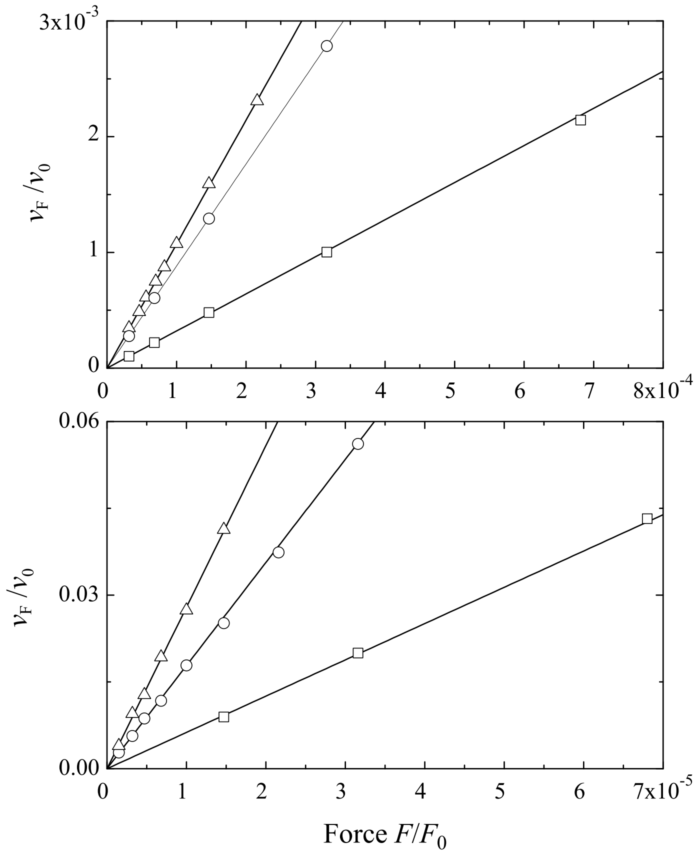
$\frac{E_B}{E_0} = 5, \frac{2\sigma}{L} = 0.5$ (cercles)

(b) $\beta E_B = 0.020$ (d) $\beta E_B = 0.70$

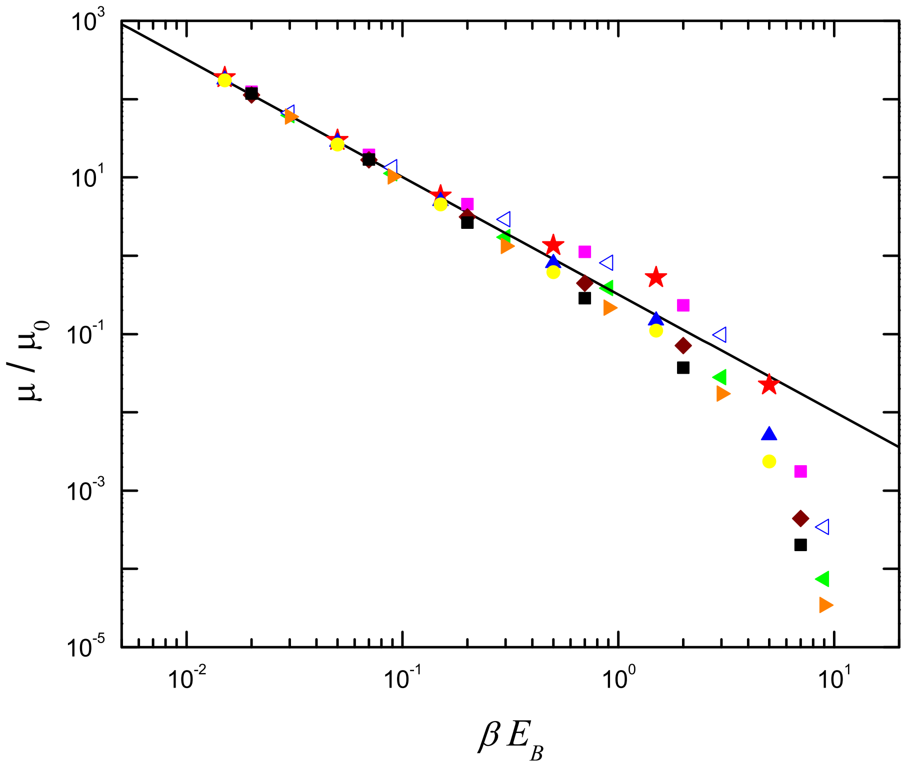
$\frac{E_B}{E_0} = 0.5, \frac{2\sigma}{L} = 2$ (diamants)

$\frac{E_B}{E_0} = 5, \frac{2\sigma}{L} = 2$ (carrés).

CONCLUSIONS The mean displacement is clearly linear in time for very long times. In addition, the mean drift speed $v_F(t)$ computed from the above data turns out to be linear in the applied field and independent of t.



CONCLUSION The low-field mobility μ is well-defined and field-independent. What is its temperature dependence?



Mobility μ as a function of βE_B for 9 parameter sets E_B and E_0, each for six different temperatures. The line is $\eta \left(\beta E_B\right)^{-3/2}$ with $\eta = 0.32$. The random walk model adapted to include the effect of the driving field explains the power law correctly. And the constant in front?

STEP 2 $F > 0$ WHAT'S THE PHYSICAL PICTURE?

Since this is a Hamiltonian system in thermal equilibrium Kubo's linear response theory should apply. At finite times it yields

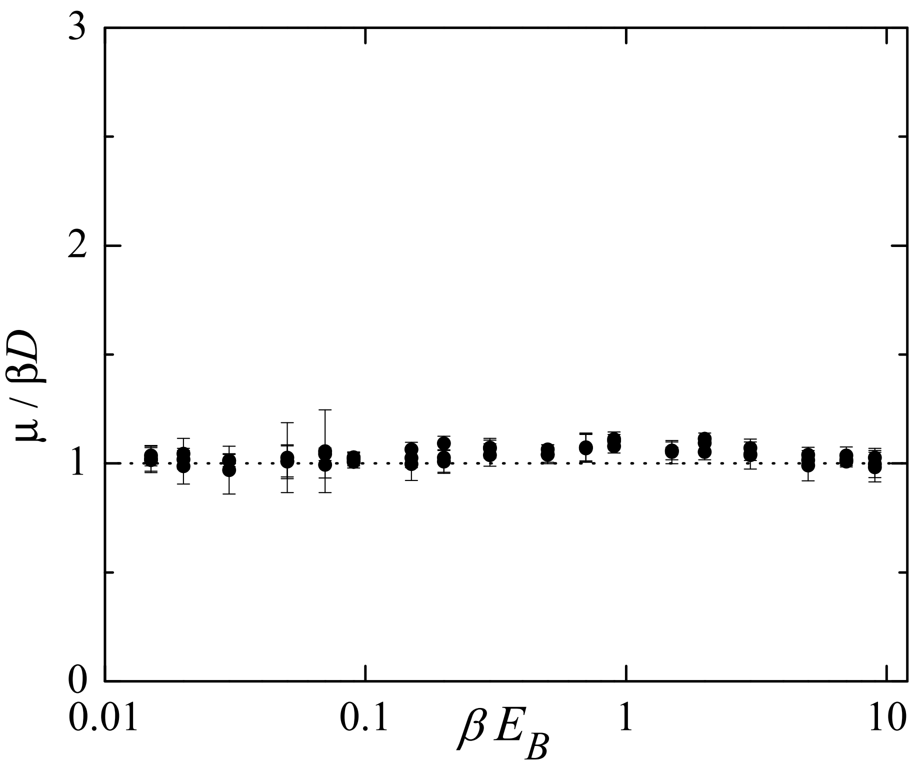
$$\frac{v_F(t)}{F} = \frac{\langle q(t,F)\rangle}{Ft} = \beta\frac{\langle q^2(t,F=0)\rangle}{2t} + \mathrm{O}_t(F).$$

Taking $F \longrightarrow 0$, the right hand side has a limit as t tends to infinity, since in absence of the field the motion is diffusive (as we showed before!!). This yields the Einstein relation:

$$\mu := \lim_{t\to\infty}\lim_{F\to 0}\frac{\langle q(t,F)\rangle}{Ft} = \beta D.$$

So the β dependence of μ should be completely determined by the one of D, which we already understand. Let's see if this works:

The Einstein relation: $\mu = \beta D$



STEP 3 $F > 0$ CONJECTURES, THEOREMS AND PROOFS

Conjecture: This system is Ohmic.

...

BUT THIS CAN’T QUITE BE TRUE (forever)

QUESTION: Does the particle reach a limiting speed v_F and is the latter linear in F, at least for small F? In other words, does the system have a well-defined low-field mobility μ that is field-independent, that is to say, is it Ohmic?

ANSWER: **NO** This can't possibly be the case. Indeed, for any $F > 0$, you should expect

$$\langle q(t, F) \rangle \sim \frac{1}{2} F t^2,$$

for large enough t.

QUESTION: Does the particle reach a limiting speed v_F and is the latter linear in F, at least for small F? In other words, does the system have a well-defined low-field mobility μ that is field-independent, that is to say, is it Ohmic?

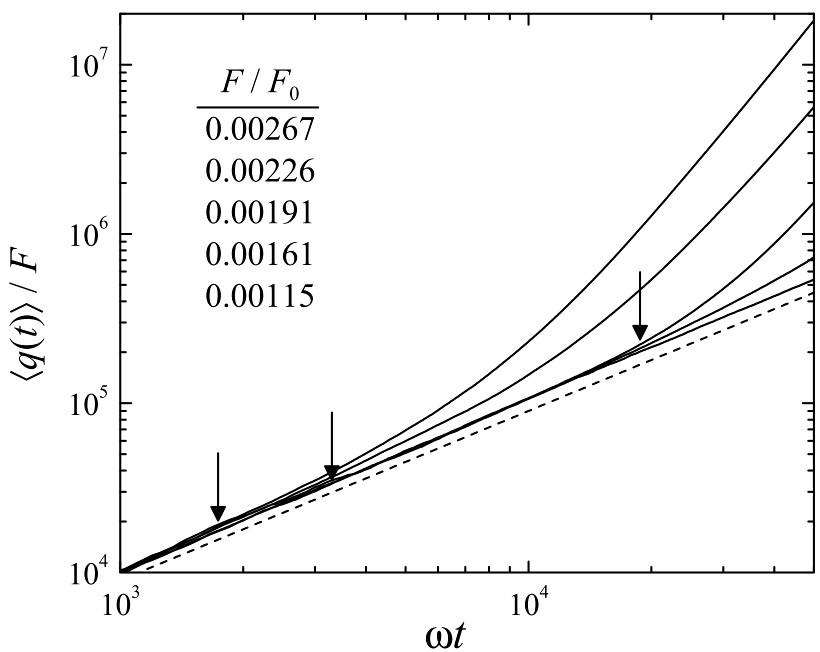
ANSWER 2: **NO** This can't possibly be true. Indeed, for any $F > 0$, you should expect $\langle q(t, F)\rangle \sim \frac{1}{2}Ft^2$, for large enough t.

WHY? The decreasing energy loss $\Delta E \sim v^{-2}$ of high speed particles to the oscillators is less than the energy Fa gained from the field: the oscillators are inefficient in slowing down fast particles. But, in a thermal distribution of particles, there are always some that are very fast, and those won't be slowed down by the oscillators. There is a time t_F beyond which their contribution to $\langle q(t, F)\rangle$ dominates and yields an asymptotic $\frac{1}{2}Ft^2$ behaviour. One can estimate

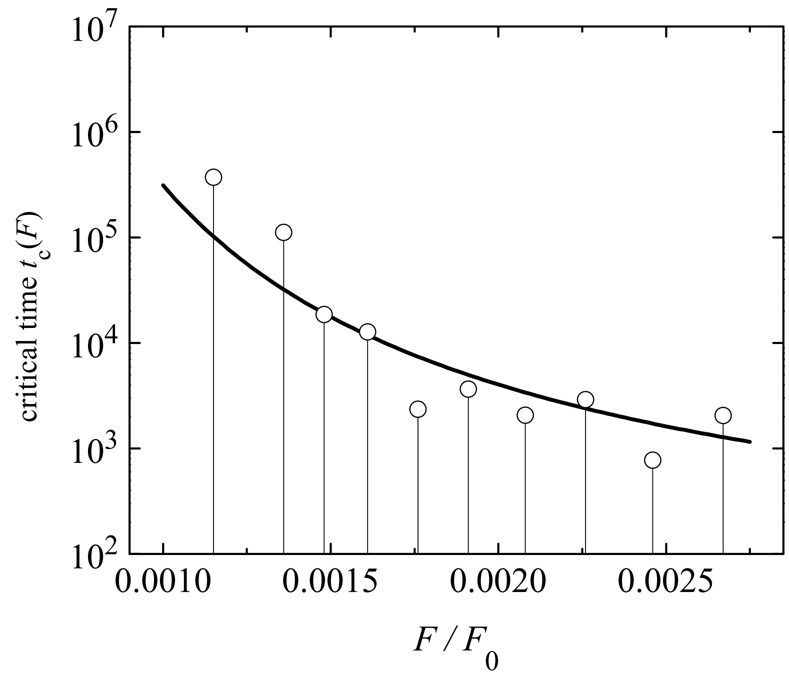
$$t_F = \frac{v_F a\sqrt{8\beta E_b E_0 \pi}}{(Fa)^{3/2}} \exp \frac{2\beta E_b E_0}{Fa} = \mu\sqrt{\frac{4\pi v_{\text{th}}}{v_F}} \exp\left(\frac{v_{\text{th}}}{v_F}\right)$$

Note: this is an ultraviolet problem: only fast oscillators can slow down fast particles.

“Seeing is believing”



$\beta E_B = 0.5, E_B/E_0 = 5, 2\sigma/L = 0.5$. Log-log plot of $\langle q_{\mathrm{S}}(t, F)\rangle/F$ against t. The parts of the graphs parallel to the dashed line correspond to behaviour linear in time. All graphs have the same mobility, as promised! But for all forces, at large times, the displacements are no longer linear in time.



$\beta E_B = 0.5,\ E_B/E_0 = 5,\ 2\sigma/L = 0.5$. Runaway times as a function of F.

$$t_F = \frac{1}{F^{1/2}} \exp(b/F).$$

BACK TO STEP 3 $F > 0$: CONJECTURES, THEOREMS AND PROOFS

QUESTION: Does the particle reach a limiting speed v_F and is the latter linear in F, at least for small F? In other words, $v_F \sim \mu F$? If so, does the Einstein relation $\mu = \beta D$ hold? In fancier terms, is linear response valid in this model, and if so, does the Kubo formula hold?

CONJECTURE: For all parameters, there exists a constant $\mu > 0$ (called the mobility) so that for times $\mu << t << t_c(F)$,

$$v_F(t) = \mu F + \mathrm{o}(F),$$

where the error term is uniform for times satisfying $\mu << t << t_c(F)$.

In this sense you get Ohmic response from a non-Ohmic bath.

PUBLICITY

The inelastic Lorentz gas, a great model to test your favourite conjectures on:

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- The role of microscopic chaos on macroscopic/thermodynamic properties
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Doing the numerics (Should someone ask!)

CHOOSE A SYSTEM: i.e. choose $2\sigma/L$ and E_B/E_0. (Nine different systems)

CHOOSE A TEMPERATURE: $10^{-2} \le \beta E_B \le 5$. (Six per system)

CHOOSE A FORCE: $10^{-5} \le F \le 10^{-2}$. (Four to ten per $2\sigma/L$, E_B/E_0, βE_B.)

RUN as many trajectories for as long as you can. ($10^3 - 10^4$ trajectories for times between 10^5 and 10^7 oscillator periods)

GOAL: determine the drift speed of the ensemble: $\langle q_{\mathrm{S}}(t, F)/t \rangle$ and compute as best you can the limit $F \longrightarrow 0$, then $t \longrightarrow \infty$.

LIMITATIONS AND DIFFICULTIES: (i) At a given time, there is a critical force F_{c} beyond which there will be breakdown (accelerated motion). Stay below F_{c}! (ii) F_{c} decreases (fast!!) if you use longer times, so need to work with very small forces. (iii) You want to take as many values of F as possible and as small as possible, but at low force, the drift is small and it is hard to get good statistics. Since you need to work at long times and small fields with large numbers of trajectories, your computers will have a hard time.