Stochastic dynamics in a continuous disordered potential

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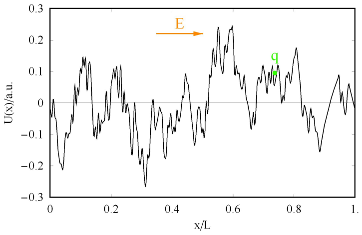
Outline

- Motivation
- Theoretical Model
- Statistical Characterization of the Potential
- Perturbation Theory
- Outlook

Motivation

- motion of mobile ions in materials with disordered structures like in amorphous and nanostructured solids:
  - ion conducting glasses
  - glass-ceramics with micro- and nanocristallite
  - ion and proton conducting polymers
- Applications
  - micro batteries
  - electrocromic window
  - chemical sensors

Theoretical Model



Langevin Equation

$$\alpha\, v = -q\,\frac{\partial}{\partial x}U(x) + q\,E(t) + F(t) \qquad (\alpha \equiv 1)$$

Statistical Properties of the Stochastic Force

$$\langle F(t)\rangle = 0, \qquad \langle F(t)F(t')\rangle = 2Q\,\delta(t-t')$$

Fokker-Planck Equation

$$\frac{\partial}{\partial t} f(x,t) = \frac{\partial}{\partial x}\left\{ q\left[\frac{\partial}{\partial x}U(x) - E(t)\right] + Q\,\frac{\partial}{\partial x}\right\} f(x,t)$$

Charge Density and Current Density

$$\begin{aligned}\rho(x,t) &= Nq\, f(x,t)\\ j(x,t) &= Nq\left\{q\left[-\frac{\partial}{\partial x}U(x) + E(t)\right] f(x,t) - Q\frac{\partial}{\partial x} f(x,t)\right\}\end{aligned}$$

Stationary Distribution for $E(t) = 0$

$$f_{E=0}(x) = f_0\, e^{-\frac{qU(x)}{Q}}\,.$$

Stationary Fokker-Planck Equation for $E(t) = E$

$$j = Nq^2 \left[-\frac{dU(x)}{dx} + E \right] f(x) - NqQ \, \frac{d}{dx} f(x)$$

Solution

$$f(x) = A \; e^{q[-U(x)+Ex]/Q} - \frac{j}{Q} \int_0^x dx' \; e^{q[-U(x)+U(x')+E(x-x')]/Q}$$

A, j are fixed by Normalization and Periodic Boundary Condition

$$\int_0^L dx \, f(x) = 1, \qquad U(x+L) = U(x) \quad \Longrightarrow \quad f(x+L) = f(x)$$

$$j(E) = \sigma(E)\, E$$

Nonlinear Conductivity

$$\sigma(E) = \frac{Nq^2}{L} \frac{\int_0^L dr\, e^{-qEr/Q}}{\int_0^L dr\, e^{K(r)-qEr/Q}}$$

$$e^{K(r)} = \frac{1}{L} \int_0^L dx\, e^{V(x,r)}$$

Potential Increment

$$V(x,r) = \frac{q}{Q} \left[U(x+r) - U(x) \right]$$

$$U(x) \equiv \text{const} \qquad \Longrightarrow \qquad j = \frac{Nq^2}{L} E = \sigma_{\text{Ohm}} E$$

Statistical Characterization of the Potential

Fourier Expansion

$$U(x) = \sum_{n=0}^{\infty} U_n \cos k_n x + V_n \sin k_n x, \qquad k_n = \frac{2\pi}{L} n.$$

$$V(x,r) = \sum_{n=1}^{\infty} U_n[\cos k_n(x+r) - \cos k_n x] + V_n[\sin k_n(x+r) - \sin k_n x]$$

Gaussian Ensemble for U_n, V_n

$$\langle U_n \rangle = \langle V_n \rangle = 0, \qquad \langle U_n U_m \rangle = \langle V_n V_m \rangle = D_n^2 \delta_{n,m}, \qquad \langle U_n V_m \rangle = 0$$

$$W(U_n, V_n) = \frac{1}{2\pi D_n^2} e^{-U_n^2/2D_n^2} \, e^{-V_n^2/2D_n^2}$$

Characteristic Functional for $V(x,r)$

$$Z_V[\eta] = \left\langle e^{i\int_0^L dr \int_0^L dx\, \eta(x,r) V(x,r)} \right\rangle$$
$$= \prod_{n=1}^{\infty} \int_{-\infty}^{\infty} dU_n \int_{-\infty}^{\infty} dV_n\, e^{iq(U_n C_n + V_n S_n)/Q}\, W(U_n, V_n)$$
$$= \prod_{n=1}^{\infty} e^{-q^2 D_n^2 (C_n^2 + S_n^2)/2Q^2}$$

$$C_n = \int_0^L dr \int_0^L dx\, \eta(x,r) \left[\cos k_n(x+r) - \cos k_n x\right]$$
$$S_n = \int_0^L dr \int_0^L dx\, \eta(x,r) \left[\sin k_n(x+r) - \sin k_n x\right]$$

n-Point Correlation Function

$$\langle V(x_1,r_1)\dots V(x_n,r_n)\rangle = \left.\frac{\delta^n Z_V[\eta]}{i^n \delta\eta(x_n,r_n)\dots\delta\eta(x_1,r_1)}\right|_{\eta(x,r)\equiv 0}$$

odd n

$$\langle V(x_1,r_1)\dots V(x_{2n+1},r_{2n+1})\rangle = 0$$

even n

$$\langle V(x_1,r_1)\dots V(x_{2n},r_{2n})\rangle = \sum_P \langle V(x_1,r_1)V(x_2,r_2)\rangle + \dots$$
$$\dots + \langle V(x_{2n-1},r_{2n-1})V(x_{2n},r_{2n})\rangle$$

Two-Point Correlation Function

$$\langle V(x_1, r_1)V(x_2, r_2)\rangle = \frac{q^2}{Q^2}\sum_{n=1}^{\infty} D_n^2 \left[\cos k_n(x_1 + r_1 - x_2 - r_2)\right.$$
$$\left. - \cos k_n(x_1 + r_1 - x_2) - \cos k_n(x_1 - x_2 - r_2) + \cos k_n(x_1 - x_2)\right]$$

$$\langle V^2(x, r)\rangle = \frac{2q^2}{Q^2}\sum_{n=1}^{\infty} D_n^2 \left[1 - \cos k_n r\right]$$

Perturbation Theory for $qEL/Q \gg K(r,Q,L)$

$$\begin{aligned} \sigma &= \sigma_{\text{Ohm}} \frac{L \int_0^L dr\, e^{-ar}}{\int_0^L dr \int_0^L dx\, e^{V(x,r)-ar}}, \qquad a = \frac{qE}{Q} \\ &= \sigma_{\text{Ohm}} \frac{L\left[1 - e^{-aL}\right]}{a \int_0^L dr \int_0^L dx\, \left[1 + \sum_{n=1}^{\infty} V^n(x,r)/n!\right] e^{-ar}} \\ &= \frac{\sigma_{\text{Ohm}}}{1 + \frac{a}{L[1-e^{-aL}]} \sum_{n=1}^{\infty} \int_0^L dr \int_0^L dx\, V^n(x,r)/n!\, e^{-ar}} \end{aligned}$$

Averaging

$$\langle\sigma\rangle = \sigma_{\text{Ohm}} \left\{ 1 + \sum_{m=1}^{\infty} \left[\frac{-a}{L[1 - e^{-aL}]} \right]^m \left\langle \left[\sum_{n=1}^{\infty} \int_0^L dr \int_0^L dx V^n(x,r)/n! e^{-ar} \right]^m \right\rangle \right\}$$

Consider only Terms up to $\langle V(x_1, r_1)V(x_2, r_2)V(x_3, r_3)V(x_4, r_4)\rangle$

$$\langle\sigma\rangle = \frac{\sigma_{\text{Ohm}}\, L \int_0^L dr\, e^{-ar}}{\int_0^L dr \int_0^L dx\, e^{-\langle V^2(x,r)\rangle/2}\, e^{-ar}} = \frac{\sigma_{\text{Ohm}}\, L \int_0^L dr\, e^{-ar}}{\int_0^L dr \int_0^L dx\, \left\langle e^{V(x,r)} \right\rangle\, e^{-ar}}$$

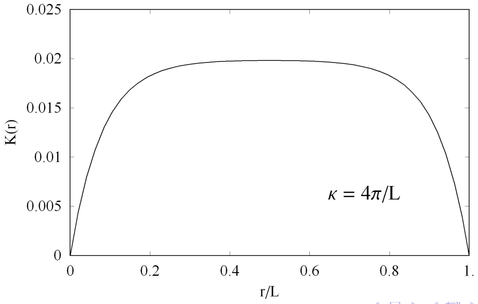
Lorentzian Distribution for Standard Deviations

$$D_n = \frac{1}{L\sqrt{k_n^2 + \kappa^2}}$$

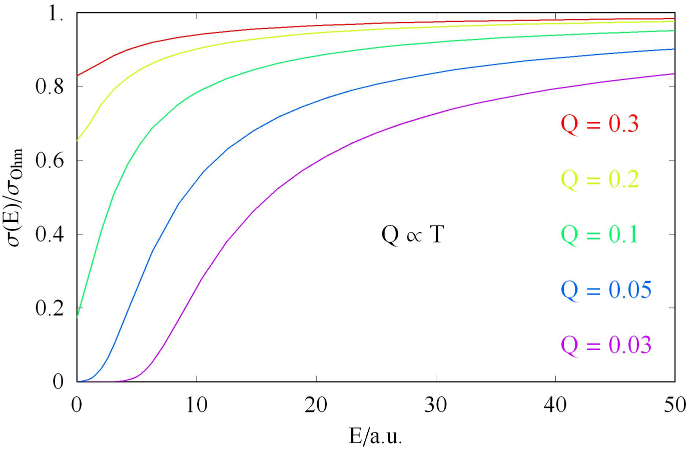
Perturbation Theory for $qEL/Q \gg K(r,Q,L)$

$$K(r) = -\frac{1}{2}\langle V^2(x,r)\rangle = \frac{q^2}{Q^2}\left[\langle U^2(0)\rangle - \langle U(r)U(0)\rangle\right]$$

$$= \frac{q^2}{4Q^2\kappa L}\,\frac{\cosh \kappa L/2 - \cosh \kappa(r - L/2)}{\sinh \kappa L/2}$$



Results


1.
0.8
0.6
0.4
0.2
0
$\sigma(E)/\sigma_{Ohm}$
0
10
20
30
40
50
E/a.u.
Q = 0.3
Q = 0.2
Q = 0.1
Q = 0.05
Q = 0.03
Q ∝ T

Perturbation Theory for small qEL/Q

Mirror Summetry wit respect to $x = L/2$

$$K(r) = K(L-r) \quad \Longrightarrow \quad \sigma(-E) = \sigma(E), \qquad j(-E) = -j(E)$$

Perturbation Expansion

$$j = \sigma_1 E + \sigma_3 E^3 + \sigma_5 E^5 + \dots$$

Coefficients

$$\sigma_1 = \frac{Nq^2}{\int_0^L dr\, e^{K(r)}}$$

$$\sigma_3 = \frac{Nq^4}{2Q^2} \frac{\int_0^L dr\, \left[L^2/12 - (r - L/2)^2\right] e^{K(r)}}{\left[\int_0^L dr\, e^{K(r)}\right]^2}$$

Standard Deviation of a Constant Function e^C

$$D_C^2 = \frac{\int_0^L dr\,(r - L/2)^2\, e^C}{\int_0^L dr\, e^C} = \frac{L^2}{12}$$

Standard Deviation of the Function $e^{K(r)}$

$$D_{K(r)}^2 = \frac{\int_0^L dr\,(r - L/2)^2\, e^{K(r)}}{\int_0^L dr\, e^{K(r)}}$$

Second Coefficient

$$\sigma_3 = \frac{q^2}{2Q^2}\left[D_C^2 - D_{K(r)}^2\right]\sigma_1.$$

Outlook

- Standard Deviation $\Delta j = \sqrt{\langle j^2 \rangle - \langle j \rangle^2}$
- Conductivity for AC $E(t) \propto \sin \omega t$