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Microscopic model for the Langevin equation: Force-force correlation function

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We look into the particle diffusion in a 1D atomic chain. We consider two different models. In the first one the lattice particles are supposed to move independently. The stochasticity of the motion in this case is achieved due to nonlinear oscillations of the lattice particles. In the second case the linear oscillations of the lattice particles are considered and the stochasticity of doping particle motion stems from the finiteness of phonon spectra. In both cases we derive the stochastic properties of the Langevin force. The found expressions for the correlation function of the Langevin force could be reduced to the white noise only at some limiting values of the lattice and thermostat parameters.

Keywords: diffusion, Langevin force, correlation function, microscopic theory.

У статті досліджується дифузія частинки в 1D ланцюжці атомів. Розглядаються дві різні моделі. У першій моделі передбачається, що частинки решітки рухаються незалежно одна від одної. Стохастичність руху в цьому випадку досягається за рахунок нелінійних коливань частинок решітки. У другому випадку розглядаються лінійні коливання частинок решітки і стохастичність руху частинки домішки пов'язана з обмеженністю фононних спектрів. В обох випадках досліджені стохастичні властивості сили Ланжевена. Знайдені вирази для кореляційної функції сили Ланжевена можуть бути зведені до білого шуму лише при деяких граничних значеннях параметрів решітки та термостата.

Ключові слова: дифузія, сила Ланжевена, кореляційна функція, мікроскопічна теорія.

В статье исследуется диффузия частицы в 1D цепочке атомов. Рассматриваются две различные модели. В первой модели предполагается, что частицы решетки движутся независимо друг от друга. Стохастичность движения в этом случае достигается за счет нелинейных колебаний частиц решетки. Во втором случае рассматриваются линейные колебания частиц решетки и стохастичность движения примесной частицы связана с конечностью фононных спектров. В обоих случаях изучены стохастические свойства силы Ланжевена. Найденные выражения для корреляционной функции силы Ланжевена могут быть сведены к белому шуму только при некоторых предельных значениях параметров решетки и термостата.

Ключевые слова: диффузия, сила Ланжевена, корреляционная функция, микроскопическая теория.

Introduction

The diffusion properties of Brownian particles continues to be of enormous interest even though a century has passed since the appearance of the famous work of Einstein on the subject [1].

A central point of Einstein's work is the insight that within the complicated many-body system, a time-scale separation exists between the particles slow center of mass and a huge number of remaining fast molecular degrees of freedom. In statistical physics the stochastic Langevin equation is often used to describe this 'slow' motion. The fast (microscopic) variables are responsible for the stochastic nature of the Langevin equation. This approach finds many applications in different branches of physics. For example, the Langevin equations are used in the statistical mechanical treatment of time-dependent phenomena in fluids [2], to describe nuclei fission and fusion [3], and in other areas of science [4].

The common model of random forces used in the Langevin approach, the so-called Langevin forces, is white noise. As a matter of fact, this phenomenological approximation imposes restrictions on the formulation of problems which could be solved by means of this model. On the other hand, the microscopic theory of statistical properties of Langevin forces highlights some new information about the stochastic nature of the Langevin model.

In this paper we look into the doping particle diffusion in a 1D chain of atoms. We consider two different models. In the first one, (Sec.2), the lattice particles are supposed to

move independently. The stochasticity of the motion in this case is achieved due to nonlinear oscillations of the lattice particles.

In the second case, (Sec.3), the linear oscillations of the lattice particles are considered and the stochasticity of doping particle motion stems from the finiteness of phonon spectra. In both cases we derive the stochastic properties of the Langevin force. It is interesting to note that the found expressions for the correlation function of the Langevin force could be reduced to the white noise only at some limiting parameter values.

Model of non-linear oscillations

a. Formulation of problem

Let us consider a particle of mass m moving in a field of 1D diatomic lattice of particles of masses M, a distance between the lattice sites is l, equilibrium positions of lattice atoms in (q,Q) plane are $(kl,\pm\bar{Q})$, $k=\ldots-1,0,1,\ldots$ (see Fig. 1). Let us introduce Q_k which stands for deviation of the k-th particle from its equilibrium position. To simplify the problem we consider only anti-phase oscillations of the nearest atoms as shown in Fig. 1. q is the coordinate of the foreign diffusion particle.

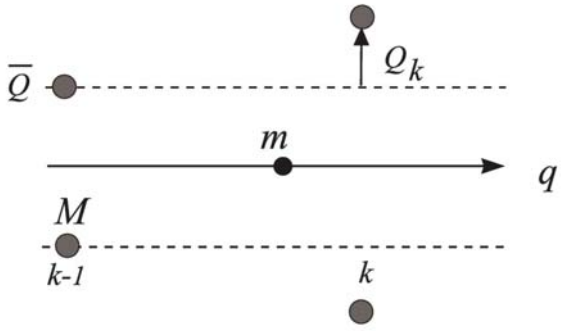

Fig. 1. The model of 1D diatomic lattice with transversal displacements.

Hamiltonian of such system in the absence of interaction between the lattice particles is given as

$$H=\frac{p^2}{2m}+\sum_k\left[\frac{P_k^2}{2M}+U(Q_k)\right]+ \\ +\sum_k U_{int}\left(q-kl,\bar{Q}+Q_k\right). \tag{1}$$

Expansion of the non-linear potential of anti-phase oscillations $U(Q_k)$ in the Taylor series up to the fourth order near the equilibrium position of the particles reads

$$U(Q)=M\left(\frac{\omega_0^2Q^2}{2}+\frac{\alpha Q^3}{3}+\frac{\beta Q^4}{4}\right). \tag{2}$$

b. Equations of motion for impurity particle

Expanding the potential of interaction between the doping particle and the lattice particles into series we obtain

$$U_{int}\approx U_{int}\big|_{Q_k=0}+\frac{\partial U_{int}}{\partial Q_k}\big|_{Q_k=0}Q_k. \tag{3}$$

The equation of motion for the particle takes the form

$$m\ddot{q}=-\sum_k\frac{\partial U_{int}}{\partial q}\big|_{Q_k=0}-\sum_k\frac{\partial^2U_{int}}{\partial q\partial Q_k}\big|_{Q_k=0}Q_k. \tag{4}$$

This equation can be solved by using the solution of the equations of motion for the lattice particles:

$$\ddot{Q}_k=\omega_0^2Q_k-\alpha Q_k^2-\beta Q_k^3+f_k(q(t)), \\ f_k(q(t))=-\frac{\partial U_{int}}{\partial Q_k}\big|_{Q_k=0}. \tag{5}$$

So we arrive at the point where we have to solve the equations of motion for the lattice particles to find a solution of the equation of motion for the doping particle.

An approximate solution of Eq. (5) can be easily found, for example, with the use of the two time scale method, see e.g. [5]. We omit this procedure and present the following solution,

$$Q_k(t)=\left(Q_{k0}+I_k(t)\right)\cos\left(\Omega_k(t-t_0)+\varphi_k\right), \\ I_k(t)=\frac{1}{\omega_0}\int_{t_0}^{t}dt'f(q(t'))\sin\left(\Omega_k(t'-t_0)+\varphi_k\right), \tag{6}$$

$$\Omega_k=\omega_0+\left(\frac{3\beta}{8\omega_0}-\frac{5\alpha^2}{12\omega_0^3}\right)|Q_{k0}|^2, \tag{7}$$

where φ_k is the initial phase of the k-th particle, Q_{k0} is its initial displacement.

Considering the last term in Eq. (4), we substitute Q_k by the corresponding expression from Eq.(6):

$$\sum_k\Phi_k(q)\left(Q_{k0}+I_k(t)\right)\cos\left(\Omega_k(t-t_0)+\varphi_k\right), \tag{8}$$

where $\Phi_k(q)=\frac{\partial^2U_{int}}{\partial q\partial Q_k}\big|_{Q_k=0}$.

This expression contains two totally different terms. The first one is the so-called Langevin force, stochastic force applied to the q-th particle; the second one is the friction force.

c. Langevin force

Consider the Langevin force:

$$F_L(q,t)=\sum_k\Phi_k(q)Q_{k0}\cos\left(\Omega_k(t-t_0)+\varphi_k\right). \tag{9}$$

Parameters Q_{k0} and φ_k are independent random variables. The first one determines the energy of the k-th particle at the moment t_0 and the second one defines the

phase of oscillations at the same moment. Also, we suppose that the system under study is in thermal equilibrium at temperature T.

Evidently, the average value of the Langevin force $\langle F_L \rangle$ equals zero. Indeed, Q_{k0} and φ_k are independent variables, so their averaging should be performed separately. The value of φ_k is distributed uniformly in the interval $0 \leqslant \varphi_k \leqslant 2\pi$. Now, the initial statement is obvious.

Pair correlation functions give a lot of information for describing a variety of physical processes. Some applications of physical system analysis based on the correlation functions can be found in [4, 6, 7]. In the present paper we consider the pair correlation function for the Langevin force, $\langle F_L(q,t)F_L(q,t')\rangle$, where the sign $\langle \ldots \rangle$ means the ensemble averaging over initial states of environment, i.e. the 1D lattice. From Eq. (9) it follows:

$$\langle F_L(t)F_L(t')\rangle = \sum_{k,k'} \Big\langle \Phi_k \Phi_{k'} Q_{k0} Q_{k'0} \times \\ \times \cos(\Omega_k (t-t_0)+\varphi_k)\cos(\Omega_{k'}(t'-t_0)+\varphi_{k'})\Big\rangle. \quad (10)$$

Herein and in what follows we omit the symbol q in the correlation function $\langle F_L(t)F_L(t')\rangle$. We consider oscillations of each pair of lattice particles independently, so that all terms with $k \neq k'$ in the double sum in Eq. (10) go to zero. It is clear that one of the terms in Eq. (10), proportional to $\cos\big(\Omega_k(t+t'-2t_0)+2\varphi_k\big)$, vanishes after averaging over φ_k. Then, we get the following result,

$$C(t) = \langle F_L(t)F_L(t')\rangle = \frac{1}{2}\sum_k \Phi_k^2 \langle Q_{k0}^2 \times \\ \times \cos\Big(\omega_0(1+\gamma Q_{k0}^2)(t-t')\Big)\rangle, \quad (11)$$

where γ is defined from Eq. (7),

$$\gamma = \frac{3\beta}{8\omega_0^2} - \frac{5\alpha^2}{12\omega_0^4}, \quad (12)$$

and Q_{k0} independence of Φ_k is taken into account. Thus, Φ_k may be taken out of the sign for average. We suppose that the initial energy of the oscillators obeys the Gibbs distribution. After averaging we have

$$\langle Q_{k0}^2 \cos\Big(\omega_0(1+\gamma Q_{k0}^2)(t-t')\Big)\rangle = \\ = A\int_0^\infty dQ_{k0}\, Q_{k0}^2 \cos\Big[\omega_0(1+\gamma Q_{k0}^2)(t-t')\Big]\times \\ \times \exp\left(-\frac{M\omega_0^2 Q_{k0}^2}{k_B T}\right), \quad (13)$$

where A is the normalization factor, $A = \sqrt{\dfrac{2\pi k_B T}{M\omega_0^2}}$.

Calculation of the integral in Eq. (13) gives

$$C(\tau) = \langle F_L(t)F_L(0)\rangle = \\ = C(0)\frac{\xi^{3/2}}{\left(\tau^2+\xi^2\right)^{3/4}}\cos\left(\tau + \frac{3}{2}\arctan\frac{\tau}{\xi}\right), \quad (14)$$

where $\tau = \omega_0 t$ is the dimensionless time, $\xi = \dfrac{M\omega_0^2}{k_B T\gamma}$ is the parameter describing the nonlinearity, $C(0) = \dfrac{A\sqrt{\pi}}{(4\gamma\xi)^{3/2}}\sum_k \Phi_k^2$ is the variance of the Langevin force.

A shape of correlation function $C(\tau)$ is determined by the parameter $\dfrac{\xi}{\omega_0}$. It is the characteristic time of correlation due to the non-linearity of interaction between the lattice particles. It is clearly seen from Fig. 2 that for the strong non-linearity (i.e. if $\xi \ll 1$) the correlation function becomes close to the delta-function, whereas in the case of linear oscillations the correlator is a periodic function. It can also be shown analytically that Eq. (14) is a pre-limit form of the delta function. If $\tau \to \infty$, correlations decrease to zero with growth of τ. On the other hand, assuming that τ comes close to zero, one can see that right hand side of Eq. (14) turns into $C(0) \sim \xi^{-3/2}$. The smaller ξ is, the closer correlations become to delta-functional. Sharpness of the delta function peak is also determined by the value of ξ and grows as $\xi^{-3/2}$.

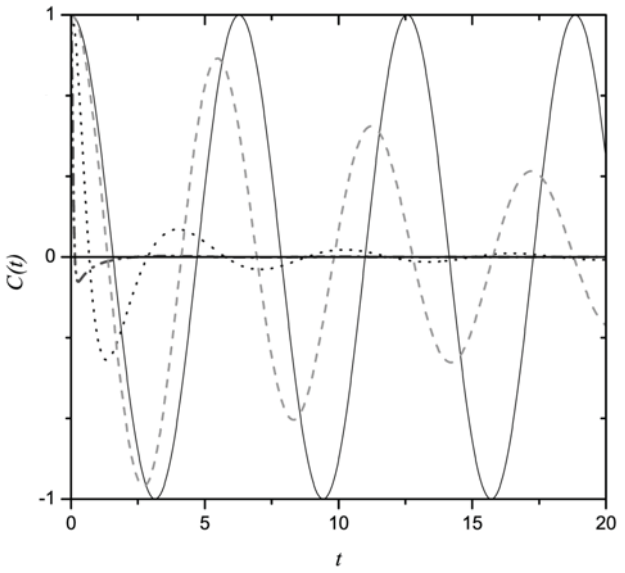

Fig. 2. The $C(t)$ dependence of the normalized correlation function of the Langevin force at different values of the parameter $\alpha = \gamma k_B T / M\omega_0^2$ ($\alpha = 0.1$, dashed line; $\alpha = 1$, dotted line; $\alpha = 10$, dash-dotted line; the case of linear oscillations corresponds to $\alpha = 0$, solid line).

We would like to mention that the correlator $C(t)$ also depends on q. It is clear that this dependence is periodic with the period l. One can see that the sharpness of the potential determines the amplitude of correlations. The more the gradient of potential along the direction of motion is, the more this motion is correlated.

In Eq. (9) all the summands are independent and normally distributed. It follows from the central limit theorem that the Langevin force distribution law is Gaussian too. The variance of its distribution is equal to the correlation function at the point $t = t'$:

$$\langle F_L^2 \rangle = \frac{\sqrt{2}\pi (k_B T)^2}{8(M\omega_0^2)^2} \sum_k \Phi_k^2. \qquad (15)$$

So we can see that the root mean square value of the Langevin force grows with the temperature as T. At high temperatures the variance of the Langevin force increases and correlation function comes closer to the delta function.

Lattice model with linear longitudinal displacement of atoms

In the model considered below, we suppose the particles of the lattice interact with the nearest neighbours only and move along the axis of 1D crystal. In this case the Hamiltonian of the system differ from the one in Eq. (1) in potential energy of the lattice atoms of the k-th site. The latter now depends not only on the displacement Q_k, but also on displacements of all the other lattice sites (which now directed along the doping particle motion).

Similarly to what has been stated in previous sections, let us first determine the motion of the lattice particles taking account of the motion of a foreign particle. To simplify the problem, assume that particles interact solely with two nearest neighbours, and the potential energy of interaction is quadratic in displacement. The lattice can then be viewed as if each lattice atom is coupled with two neighbours via springs with equal force K, as shown in Fig. 3. This reduces the formulated problem to the well known one pertinent to the dynamics of the linear chain of coupled oscillators.

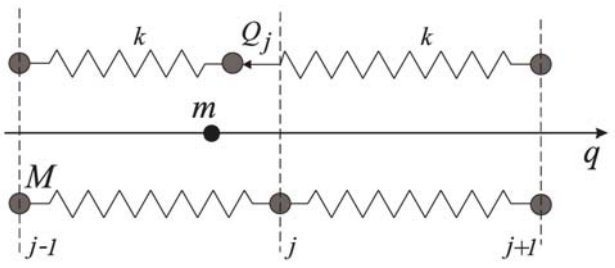

Fig. 3. Model of 1D lattice with longitudinal displacements.

Equation of motion for the k-th oscillator now reads as

$$M\ddot{Q}_k = K(Q_{k-1} + Q_{k+1} - 2Q_k). \qquad (16)$$

Looking for the solution of Eq. (16) in the form of the travelling wave $Q_k = A\exp\left(i(\omega t - \varkappa k)\right)$, we obtain the following dispersion equation:

$$M\omega^2 = K\left(2\sin\frac{\varkappa}{2}\right)^2. \qquad (17)$$

We choose the cyclic boundary conditions, i.e. $Q_0 = Q_N$, which is equivalent to $\exp(i\varkappa N) = 1$. It means that $\varkappa$ takes on the discrete set of values:

$$\varkappa_l = \frac{2\pi l}{N} = \frac{2\pi l a}{L}, \qquad (18)$$

where a is the distance between neighbouring atoms (the lattice period), L stands for a characteristic length of the crystal.

So, oscillations of each lattice particle appear to be the superposition of the obtained standing waves. Since the initial time moment and the initial coordinate are arbitrary, Eq. (16) can be rewritten as follows:

$$Q_k = \sum_{l=1}^{N-1} A_l \sin(\omega_l t + \varphi_l)\cos(\varkappa_l k). \qquad (19)$$

The summation starts with $l = 1$ because we do not make allowance for the motion of the lattice as a whole. Parameters and φ_l are independent stochastic values. A_l is distributed according to the Gibbs law, and φ_l is uniformly distributed within the interval $(0, 2\pi)$.

The doping particle affects the motion of lattice particles which leads to the addition of summand in Eq. (19):

$$Q_k = \sum_{l=1}^{N-1} A_l \sin(\omega_l t + \varphi_l)\cos(\varkappa_l k) + G(t). \qquad (20)$$

We do not consider an exact expression for $G(t)$, because we are interested only in the stochastic component of Q_k. The equation of motion for the doping particle is the same as Eq. (4), so the expression for the Langevin force is

$$F_L(q,t) = \sum_{k,l} \Phi_k(q) A_l \sin(\omega_l t + \varphi_l)\cos(\varkappa_l k). \qquad (21)$$

One can see that the summation over coincides with the Fourier transform. Introducing the new notation $\hat{\Phi}_\varkappa = \sum_k \Phi_k \cos(\varkappa k)$, we obtain

$$F_L(t) = \sum_l \hat{\Phi}_{\varkappa_l} A_l \sin(\omega_l t + \varphi_l). \qquad (22)$$

Using the expression for the Langevin force, Eq.(22),

we can derive the expression for its correlation function:

$$\langle F_L(t)F_L(t')\rangle = \langle \sum_{l,l'} \hat{\Phi}_{\varkappa_l} \hat{\Phi}_{\varkappa_{l'}} A_l A_{l'} \times \times \sin(\omega_l t + \varphi_l)\sin(\omega_{l'} t' + \varphi_{l'})\rangle. \quad (23)$$

It is evident that $\langle A_l \rangle = 0$, $\langle A_l A_{l'} \rangle = 0$, $\langle A_l^2 \rangle = \frac{k_B T}{m\omega_l^2}$.

Thus,

$$\langle F_L(t)F_L(t')\rangle = \sum_l \hat{\Phi}^2_{\varkappa_l} \frac{k_B T}{m\omega_l^2} \cos\left(\omega_l (t-t')\right). \quad (24)$$

Using Eq. (17) we can calculate the sum in Eq. (24).

So, we have obtained the expression for the correlation function of the Langevin force in the case of interacting lattice particles. To calculate correlation function (24), we can replace the sum in Eq. (24) by the integral (as in [3]). The plot of this function is presented in Fig. 4. One can then note that the correlation function becomes a delta function if the spectral density of oscillations is quadratic.

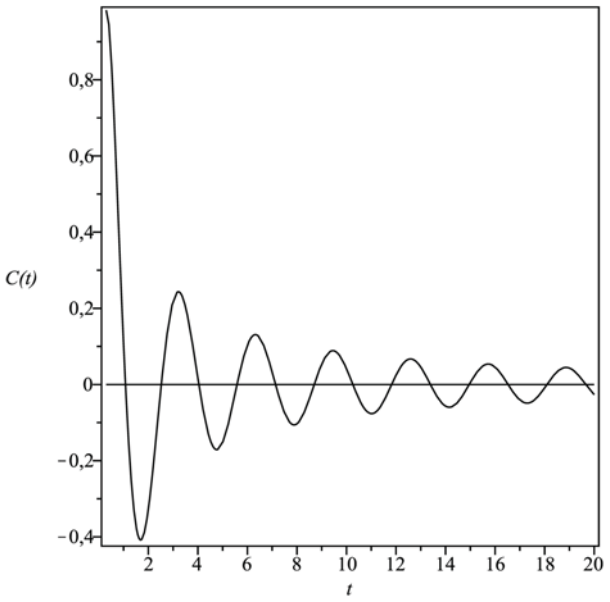

Fig. 4. The normalized correlation function of the Langevin force in approximation of linear longitudinal oscillations.

The right-hand side of Eq. (22), as in Sec.2c, is a sum of independent Gaussian distributed random values. Consequently, the Langevin force (22) is normally distributed too.

In conclusion, we should emphasize that the pair correlation function of the Langevin force plays a great role in determining the doping particle motion. So, the equations obtained are very important for the solution of the diffusion problem.

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