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Self-diffusion in clusters

An analytical model and its verification by molecular dynamics simulations

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Abstract. In this paper we propose a new analytical model for diffusion in a condensed system that describes the process in terms of the dynamics of the system on the potential energy surface (PES). Theoretical predictions are compared with the results of molecular dynamics (MD) simulations for the Lennard–Jones (LJ) clusters and show good agreement with them.

PACS. 36.40.-c Atomic and molecular clusters – 66.10.-x Diffusion and ionic conduction in liquids – 66.30.-h Diffusion in solids

1 Introduction

There exists a variety of systems of different physical natures (atomic and molecular clusters, "dust crystals", polymers, biomolecules, etc.), which are remarkably similar from the point of view of their dynamics in potential energy surface (PES) terms. Furthermore, from this point of view there is no essential difference between finite and macroscopic systems. Typically, the PES consists of a large number of the potential wells which are connected by the saddle-point valleys. Each of the wells, or more specifically, its minimum, corresponds to a certain mechanically stable atomic configuration which represents one of the inherent structures of the system (in the case of clusters, we call these structures isomers). Depending on the temperature, such systems usually show either solid-like or liquid-like behavior. Therefore, we will refer to them as to condensed systems.

In recent years, much attention has been given to the dynamics of complex systems on the PES [1–9]. The prime objective has been to derive a master equation which would allow one to study a system's dynamics at large time scales, when many inherent structures are involved [1–6]. Another important objective is the modification of the conventional methods of direct simulation (molecular dynamics (MD) and Monte Carlo) for this purpose [8, 9].

A specific realization of a system's dynamics at large time scales is the process of diffusion (or of self-diffusion, for systems of identical particles). A challenging problem which still exists here is finding a unified description of the process for the solid-like and liquid-like states (both for the bulk matter [10, 11] and for clusters [12–14]). It is tempting to address this problem in PES terms.

In this paper, we adopt the known scenario of diffusion: The system dwells for a while in a potential well and then leaves it for another well. This has been considered by Zwanzig [11] in application to the bulk liquid in particular. We propose, however, a new formalism for this scenario, which is somewhat similar to the formalism previously used in [15] for considering rotational diffusion in liquids. Specifically, we suppose that each of the potential wells is characterized by a certain dependence of the mean square displacement (MSD) of the atoms on time. At small times, this dependence corresponds to the ballistic motion of the atoms, whereas at large times it is saturated because of the finite size of the wells. Then the total displacement of the atoms in the system is a sum of the contributions of the wells; in each of them, lifetimes follow a certain distribution. A difference between the solid-like and liquid-like states is that for the former, the system predominantly resides in the wells in a waiting regime, whereas for the latter, it passes the wells in the ballistic regime, or close to this regime. An attractive feature of this formalism is that it offers an apparent way for the correlation between the system's motions in different wells, which plays a key role for the liquid-like state, to be taken into account. Theoretical predictions are verified by the MD simulations for the Lennard–Jones (LJ) clusters.

2 The model

Let the system visit the potential wells with the numbers $i = 1, ..., k$ for the time t; the system resides in each of the wells for the time $\tau_1, ..., \tau_k$, respectively (Fig. 1). To simplify things, we assume all the wells to be identical, so that the residence time in each of them is distributed according

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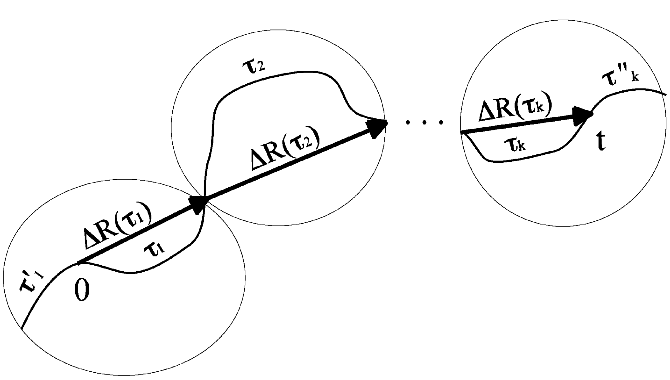

Fig. 1. Schematic picture of system's dynamics on the PES.

to the same probability density $p(t)$ ($\int_0^\infty p(t)\,\mathrm{d}t = 1$). The initial moment, when we start watching the system ($t = 0$), may not coincide with the moment when the system enters the first well, and the last moment of the watching interval (t) may be different from the moment the system leaves the kth well. Because of this, the total residence time of the system in these wells will be $\tau_1' + \tau_1$ and $\tau_k + \tau_k''$, respectively. Thus, in the sequence of the events with the probability density

$$\begin{aligned} P(\tau_1', \tau_1, \tau_1'') &= p(\tau_1 + \tau_1' + \tau_1'') \\ P(\tau_1', \tau_1, ..., \tau_k, \tau_k'') &= p(\tau_1 + \tau_1')p(\tau_2)... \\ &\quad \times p(\tau_{k-1})p(\tau_k + \tau_k''), \quad k > 1, \end{aligned} \tag{1}$$

we will be interested in the events corresponding to all possible positive $\tau_1', \tau_1, ..., \tau_k, \tau_k''$ at $\tau_1 + \tau_2 + ... + \tau_k = t$.

The current radius of the system in configuration space, counted from the point corresponding to $t = 0$, is $\mathbf{R}(t) = \{x_1(t), x_2(t), ..., x_{3n}(t)\}$, where n is the number of atoms in the system, and $x_i(t)$ are the atomic coordinates. It can be written as $\mathbf{R}_{\tau_1,...,\tau_k} = \sum_{i=1}^{k} \Delta\mathbf{R}(\tau_i)$, where $\Delta\mathbf{R}(\tau_i)$ is the change of $\mathbf{R}(t)$ in the ith well. Then the MSD corresponding to $\mathbf{R}_{\tau_1,...,\tau_k}$ is

$$\begin{aligned} R^2_{\tau_1,...,\tau_k}(t) = &\sum_{1 \le i \le k} \left\langle \Delta R^2(\tau_i) \right\rangle \\ &+ 2 \sum_{1 < i \le k} \sum_{j < i} \left\langle \Delta\mathbf{R}(\tau_i) \cdot \Delta\mathbf{R}(\tau_j) \right\rangle, \end{aligned} \tag{2}$$

where the corner brackets indicate the averages over a subset of the phase trajectories, which are possible for the given sequences of the wells and residence times under the conditions under consideration (e.g., at a constant total energy or at a constant temperature).

The quantity $\Delta\mathbf{R}(\tau_i) \cdot \Delta\mathbf{R}(\tau_j)$ in the second term of the right-hand side of (2) can be written as $\Delta R(\tau_i)\Delta R(\tau_j) \cos\Theta_{ij}$, where Θ_{ij} is the angle between the vectors $\Delta\mathbf{R}(\tau_i)$ and $\Delta\mathbf{R}(\tau_j)$ (see Fig. 1). Since $\langle\cos\Theta\rangle = 0$ at a uniform random scattering, the first term in the right-hand side of (2) can be associated with such events. Then the function of the second term is to take into account the angular correlations between the $\Delta\mathbf{R}(\tau_i)$ segments for different wells, primarily in the range of small angles, where $\langle\cos\Theta\rangle \simeq 1$.

To calculate $R^2_{\tau_1,...,\tau_k}$, we assume the following:

(i) within a well,

$$\left\langle \Delta R^2(\tau) \right\rangle = R_0^2(\tau), \tag{3}$$

where $R_0(\tau)$ is a function which corresponds to the ballistic motion of the atoms at $\tau \to 0$, and tends to a finite value as $\tau \to \infty$; and

(ii) between the wells,

$$\langle \Delta\mathbf{R}(\tau_i) \cdot \Delta\mathbf{R}(\tau_j) \rangle = R_0(\tau_i)R_0(\tau_j)Q(\tau_i)...Q(\tau_j), \tag{4}$$

where $i < j$, and $Q(\tau)$ is a function which describes how the direction of the trajectory changes within a single well. Equation (4) implies, in particular, that we assume

$$\langle \cos\Theta_{ij} \rangle = Q(\tau_i)...Q(\tau_j), \tag{5}$$

i.e., that the change in the direction of the trajectory can be described as a successive angular scattering of the trajectory by the individual wells.

Averaging $R^2_{\tau_1,...,\tau_k}$ over all possible sequences of the wells and also over all possible residence times yields

$$\begin{aligned} R^2(t) = &\frac{1}{\tau_r} \sum_{k=1}^{\infty} \underset{\substack{\tau_1+\tau_2+...+\tau_k=t \\ \tau_1',\tau_1,...,\tau_k,\tau_k''>0}}{\int \cdots \int} R^2_{\tau_1,...,\tau_k}(t) \\ &\times P(\tau_1', \tau_1, ..., \tau_k, \tau_k'')\ \mathrm{d}\tau_1'\,\mathrm{d}\tau_1 ... \mathrm{d}\tau_k\,\mathrm{d}\tau_k'', \end{aligned} \tag{6}$$

where $\tau_r = \int_0^\infty \mathrm{d}\tau \int_\tau^\infty p(\tau_1)\,\mathrm{d}\tau_1 = \int_0^\infty \tau p(\tau)\,\mathrm{d}\tau$ is the mean residence time. Then, inserting (1)–(4) into the right-hand side of (6) and applying the Laplace transformation to the result, we eventually arrive at the equation which defines the velocity autocorrelation function (VAF) of the system $C(t) = \sum_{i=1}^{n} \langle \mathbf{v}_i(t_0) \cdot \mathbf{v}_i(t_0 + t) \rangle$ ($\mathbf{v}_i$ is the velocity of the ith atom) in terms of the functions $R_0(t)$, $Q(t)$ and $p(t)$ for a single well:

$$\begin{aligned} L\left[C(t)\right] = &\frac{1}{\tau_r} L \left[C_0(t) \int_t^\infty f(\tau)\,\mathrm{d}\tau \right] \\ &+ \frac{1}{\tau_r} \frac{\left\{ L\left[\frac{\mathrm{d}}{\mathrm{d}t}\left[R_0(t)Q(t)\right] f(t) \right] \right\}^2}{1 - L\left[Q(t)p(t)\right]}, \end{aligned} \tag{7}$$

where $L[\cdot]$ is the Laplace transform, $f(t) = \int_t^\infty p(\tau)\,\mathrm{d}\tau$ is the survival probability, and $C_0(t) = (1/2)(\mathrm{d}^2/\mathrm{d}t^2)R_0^2(t)$ is the VAF for a single well. Correspondingly, the power spectrum is calculated as $I(\omega) = 2\int_0^\infty C(t)\cos(\omega t)\,\mathrm{d}t$, and the MSD as $R^2(t) = 2\int_0^t \mathrm{d}t_1 \int_0^{t_1} C(t_2)\,\mathrm{d}t_2$.

In the simplest case, when one neglects the angular correlations ($Q(t) = 0$) and assumes the Poisson distribution for $p(t)$, (7) transforms into the relation $C(t) = C_0(t)\exp(-\nu t)$, corresponding to the Zwanzig theory [11].

Finally, for the self-diffusion coefficient, which can be calculated as $D=\int_0^\infty C(t)\,\mathrm{d}t/3n=I(0)/6n$, we have

$$D=\frac{1}{3n\tau_r}\left\{\int\limits_0^\infty R_0^2(t)p(t)\,\mathrm{d}t+\frac{\left[\int\limits_0^\infty R_0(t)Q(t)p(t)\,\mathrm{d}t\right]^2}{1-\int\limits_0^\infty Q(t)p(t)\,\mathrm{d}t}\right\}.$$

In their general features, the functions $R_0(t)$, $Q(t)$ and $p(t)$ are expected to be common to all condensed systems. At the same time, it is unlikely that there exist analytical relations for them that are able to describe any specific system in every essential detail. Therefore, we introduce some "basic" relations for $R_0(t)$, $Q(t)$, and $p(t)$, which reproduce these functions in the most important features and can serve as a basis for their further specification:

1. $R_{0\mathrm{b}}^2(t)=V^2t^2/(1+t^2/a^2)$, where $V^2=2E_{\mathrm{kin}}/m$ (E_{kin} is the mean kinetic energy of the system, and m is the atomic mass), and $a^2=R_{0\infty}^2/V^2$, where $R_{0\infty}^2$ is the maximum value of the MSD within a single well. At $t\to 0$, $R_{0\mathrm{b}}^2(t)=V^2t^2$ (the ballistic motion of the atoms), and at $t\to\infty$, $R_{0\mathrm{b}}^2(t)=R_{0\infty}^2$. Correspondingly, $C_{0\mathrm{b}}(t)=V^2(1-3t^2/a^2)/(1+t^2/a^2)^3$ and $I_{0\mathrm{b}}(\omega)=\pi V^2a^3\omega^2\exp(-a\omega)/2$.

   Note that V^2 and $R_{0\infty}^2$ are the extensive quantities, being proportional to the number of vibrational degrees of freedom (it is assumed that the system executes no overall translation and rotation). Therefore, the parameter a is an intensive quantity, i.e., it is independent of the system size. It should also be mentioned that V and $R_{0\infty}$ (and, consequently, a) depend on the thermodynamics conditions, in particular, on the total energy (or the temperature) for a free system.
2. $Q_{\mathrm{b}}(t)=\exp(-q^2t^2/2)$, where q is an intensive parameter depending, again, on the thermodynamics conditions. The reasoning behind this form of $Q_{\mathrm{b}}(t)$ is as follows.

   At large residence times, the system may randomly leave the well in an arbitrary direction, i.e., its trajectory is scattered by the wells uniformly ($\langle\cos\Theta\rangle\to 0$). Corresponding with this is $Q_{\mathrm{b}}(t)\to 0$ at $t\to\infty$.

   At small residence times, the system passes the wells in the ballistic regime, or in a regime close to it. As a result, a near-forward scattering prevails, for which $\langle\cos\Theta_{ij}\rangle\simeq 1-\left\langle\Theta_{ij}^2\right\rangle/2$. Since the acceleration of the system is approximately constant at small times, the change in the direction of the trajectory within a single well is proportional to τ, i.e., $\Delta\Theta=q\tau$, where q is a constant. Then, taking into account that the trajectory is supposed to be randomly scattered, for the sequence of the wells $i,...,j$, we can write $\left\langle\Theta_{ij}^2\right\rangle=q^2\sum_{k=i}^{j}\tau_k^2$, or $\langle\cos\Theta_{ij}\rangle\simeq 1-q^2/2\sum_{k=i}^{j}\tau_k^2$. For $Q_{\mathrm{b}}(t)\simeq 1-q^2t^2/2$ at small t, this latter equation is consistent with (5). The value of the parameter q is of the order of the inverse of the time corresponding to the end of the ballistic regime.
3. $p_{\mathrm{b}}(t)=1/\nu\exp(-\nu t)$, which is the Poisson distribution. Correspondingly, the survival probability is $f_{\mathrm{b}}(t)=\exp(-\nu t)$. Because we consider the dynamics of the system in the configuration space, the frequency ν relates to the whole system rather than to a single atom. Therefore it is an extensive quantity.

To conclude this section, we note that the model is consistent with the thermodynamics limit ($n\to\infty$); this can easily be verified by substitution of the given basic relations into the derived equations. In particular, the self-diffusion coefficient is an intensive quantity.

3 Verification of the model by molecular dynamics simulations and brief discussion

To verify the model, we have conducted the constant-energy MD simulations for a set of the LJ clusters (for the computational background, see [16]). Below we present some results for 13-atom clusters as an example.

When simulating diffusion in the conventional way [12–14], one obtains data which represent some averages taken over a variety of the isomers. Since the number of geometrically different isomers (possessing different characteristics) is large, a comparison of the model with the simulation data turns out to be a real challenge: On one hand, consideration of all essential isomers is impractical, and on the other hand, introducing some average values of the parameters into the model, which would effectively account for different characteristics of the isomers, may disguise possible defects of the model.

Because of this, we first considered a subsystem of the LJ$_{13}$, which consists of permutational copies of the ground-state isomer. These copies (the icosahedra with energies $U=-44.3268$) are directly connected through the transition states (the decahedra, $U=-41.5552$; here and below, all values are given in the LJ units) [17]. Therefore, in the given subsystem, the self-diffusion is possible. On the other hand, all the isomers are geometrically identical; this corresponds exactly to the previously given formulation of the model.

To investigate this subsystem, we applied the technique recently developed in [16], which makes it possible to confine the MD trajectory to a specified catchment area on the PES; in this case, to the area consisting of the wells for the ground-state isomer permutational copies. Typical results are shown in Fig. 2.

Initially, the system was confined to the catchment basin corresponding to a single copy, and the distributions $R_0^2(\tau)$ and $f(\tau)$ were calculated (Figs. 2a,b). The first thing immediately seen from these distributions is the sharp increase in $f(\tau)$ (and thus in $p(\tau)$) at $t\to 0$, which is not consistent with the Poisson law. Such a singularity has previously been observed in the LJ clusters [16,18–20]. The origin of it is that the system ballistically crosses the wells in the neighborhood of the saddle points of high order [16]. It is also pertinent that, at least for the conditions of [16,18–20], the width of the wave packet is greater than the characteristic length of the region of the PES to which the

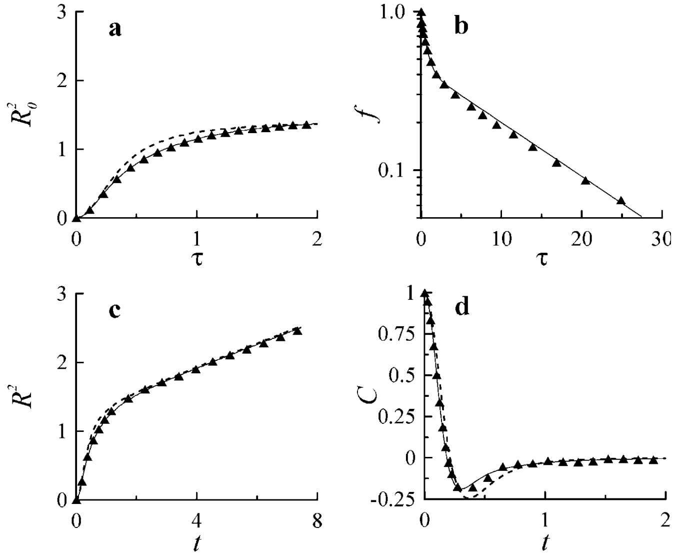

Fig. 2. Self-diffusion in the subsystem of the ground-state isomers (LJ_{13}, $E = 15$); for the definitions of the plotted functions, see the text. The symbols and lines correspond to the computer simulations and theory, respectively. In all cases, $q = 6.67$, and $\nu_1 = 1.64$, $\nu_2 = 0.078$, $\alpha_1 = 0.56$, and $\alpha_2 = 0.44$ for $p(\tau)$. The dashed line is the one-mode approximation for $R_0^2(\tau)$ ($V^2 = 10.7$, $a = 0.36$), and the solid line is the two-mode approximation ($V^2 = 10.7$, $a_1 = 0.29$, $a_2 = 0.84$, $\alpha_1 = 0.91$, and $\alpha_2 = 0.09$). The VAF (panel d) is normalized by division by $C(0) = V^2$.

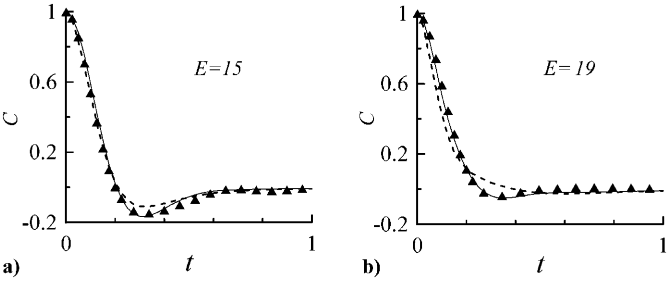

Fig. 3. The normalized VAFs for LJ_{13}. The symbols stand for the computer simulation results, and the lines for the theoretical predictions. The solid and dashed lines correspond, respectively, to the taking into account and neglect of the scattering of the MD trajectory into small angles (for the solid lines $q = 6.67$ for both $E = 15$ and $E = 19$, and for the dashed lines $Q(t) = 0$). The following two-mode approximations are used: $E = 15$: $\nu_1 = 87$, $\nu_2 = 1.3$, $\alpha_1 = 0.15$, $\alpha_2 = 0.85$ for $p(\tau)$, and $V^2 = 9.62$, $a_1 = 0.33$, $a_2 = 1.56$, $\alpha_1 = 0.92$, $\alpha_2 = 0.08$ for $R_0^2(\tau)$; $E = 19$: $\nu_1 = 115$, $\nu_2 = 2.37$, $\alpha_1 = 0.22$, $\alpha_2 = 0.78$ for $p(\tau)$, and $V^2 = 11.2$, $a_1 = 0.21$, $a_2 = 0.78$, $\alpha_1 = 0.53$, $\alpha_2 = 0.47$ for R_0^2.

singularity can be related; therefore, it may be a peculiarity of the classical approach.

To account for this singularity, we used a two-mode Poisson distribution $p(\tau) = \alpha_1 p_{b1}(\tau) + \alpha_2 p_{b2}(\tau)$, where $\alpha_1 + \alpha_2 = 1$, and $p_{b1}(\tau)$ and $p_{b2}(\tau)$ are characterized by different values of ν. A similar relation holds for $f(t)$. The result of this approximation is shown in Fig. 2b by the solid line.

In contrast to the residence times, the distribution of R_0^2 is reproduced by the basic function $R_{0b}^2(\tau)$ reasonably well (the dashed line in Fig. 2a). Nevertheless, to achieve a close approximation, it turned out to be necessary to use a two-mode representation again, one similar to that for the residence times (the solid line in Fig. 2a). The modes were characterized by different values of a, but by the same value of V. Presumably, these two different modes in R_0^2, and so in the VAF, can be related to either the bulk and surface components of diffusion, or to two different modes of atomic vibrations, which in the case of the bulk matter, correspond to the longitudinal and transverse sound velocities [11].

For $Q(\tau)$, we used its basic form $Q_b(\tau)$.

With these analytical approximations in hand, we were able to calculate all desirable quantities and compare them with those obtained by the direct MD simulations. The results are shown in Fig. 2c,d. The theoretical curves take into account the angular correlations ($Q(\tau) \neq 0$). However, since the system resides in the well in a waiting regime (the mean residence time is about 6.0, when $R_0^2(\tau)$ is saturated at $\tau \simeq 2.0$; see the panels a and b of Fig. 2, the result is practically independent of a specific value of q, and it is very close to that for $Q(\tau) = 0$.

The next step was to apply the derived equations to the conventional case, i.e., to the system freely exploring the PES. Again, for every total energy, the distributions $R_0^2(\tau)$ and $p(\tau)$ for individual wells were calculated and fitted by two-mode distributions as before, except that they were averaged over all the wells visited by the system. Figure 3 shows the VAFs of the system for two values of the total energy ($E = 15$ and $E = 19$). The first energy falls into the melting transition range, and the second one corresponds to the well developed liquid-like state (see, e.g., [12]). It is seen that in contrast to the melting transition range (and, as it should be, to the solid-like state) for the liquid-like state, the neglect of the angular correlations has a dramatic effect on the VAF (the dashed curve in the right-hand panel): First, the VAF is no longer an even function at $t = 0$ (as it has to be), and secondly, the characteristic minimum in it disappears.

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