Generalized Langevin-equation approach to impurity diffusion in solids: Perturbation theory

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We derive, from a microscopic viewpoint, a nonlinear and non-Markovian Langevin equation to describe impurity diffusion in solids, assuming weak interaction between an impurity and the host-lattice atoms. The memory function and the periodic potential in the Langevin equation are calculated for the isotropic Debye lattice which models the host crystalline solid. The diffusion constant is obtained in a closed form with the use of a theory for noise-induced activation processes.

I. INTRODUCTION

Atomic diffusion in solids has important implications in many branches of material science,[1] and there has been renewed interest in this field in connection with the rapid transport of ions in superionic conductors and the hydrogen diffusion in metals.[2] Among various theoretical models to deal with mass transport in solids, a hopping model[3,4] plays a central role in which the mean residence time τ_r on an atomic site is assumed to be much longer than the jumping time τ_j and the (tracer) diffusion constant is calculated with use of a random-walk theory, a kinetic theory, or computer simulations.[1,3,4] The hopping rate $1/\tau_r$, an important parameter in the model, is calculated from a microscopic viewpoint based on the transition-state theory[5] (TST) or the dynamical theory (DT) of the rate process.[6]

To investigate ionic motion in superionic conductors, Fulde *et al.*[7] proposed, in 1975, a continuous diffusion model in which a diffusing ion was assumed to perform Brownian motion in a periodic potential $V_p(X)$ produced by the host crystal. They used the Langevin equation of the form

$$\dot{P}=dP/dt=-\int_0^t ds\, K(t-s)P(s) - \partial V_p(X)/\partial X+F(t)\ , \tag{1}$$

where $P=M\dot{X}$; M denoting the mass of the diffusing ion. The random force $F(t)$, which satisfies the fluctuation-dissipation theorem (FDT)

$$\langle F(t)F\rangle = Mk_BTK(t)\ , \tag{2}$$

was assumed to be white and the potential to be sinusoidal

$$K(t)=2\zeta\delta(t)\ , \tag{3a}$$

$$V_p(X)=U\cos(2\pi X/a)\ . \tag{3b}$$

Because of the simplicity and the intimate relation to the hopping model in case of large friction constant at low temperature,[3] the model and the extension thereof have been studied by many authors.[3,8] One point to be noticed here is that the periodic potential and the random force, as specified by Eq. (3), are introduced phenomenologically without recourse to microscopic properties of the system.

As is well known, atomic jump events result from complex interplay between the diffusing atom and the surrounding crystalline solid and it is highly desirable if one could derive a Langevin equation like Eq. (1) from a microscopic consideration. Recently we proposed a general theory of self-diffusion in liquids and solids with use of a linear-response method.[9] When applied to diffusion of an impurity put in a host lattice, it yielded a Langevin equation of the form of Eq. (1), together with microscopic expressions for $V_p(X)$ and $K(t)$. For example, the memory function $K(t)$ was expressed in terms of the dynamic structure factor of the lattice and the self-correlation function of the impurity. However, the random force $F(t)$, which was *assumed* to satisfy Eq. (2), was introduced in an *ad hoc* manner into equation of motion of the impurity based on a physically plausible argument.

The aim of the present paper is first to give a rigorous stochastic description for impurity diffusion in solids, thus putting the Langevin theory on a firm theoretical basis, and secondly to calculate the diffusion constant with the aid of theories for the thermal activation rate of both Markovian and non-Markovian stochastic processes. For this purpose we first define our model Hamiltonian to deal with impurity diffusion in solids (Sec. II) and develop a second-order perturbation theory, regarding the interaction between the impurity and the host-lattice atoms as weak. Here we employ the exact Langevin theory by Mori[10] (Sec. III). We then apply the result to a simple lattice (a Debye model) to obtain analytic expressions for the periodic potential, the memory function, and the diffusion constant (Sec. IV). Section V contains some remarks

II. MODEL

We consider an impurity moving through interstitial sites of a harmonic lattice consisting of N atoms each with mass M. The lattice Hamiltonian is given by[11]

$$H_L=\tfrac{1}{2}\sum_{\mathbf{k},j}[\dot{Q}(\mathbf{k},j)\dot{Q}^*(\mathbf{k},j) + \omega^2(\mathbf{k},j)Q(\mathbf{k},j)Q^*(\mathbf{k},j)]\ , \tag{4}$$

where the asterisk means complex conjugate and $\omega(\mathbf{k},j)$ and $Q(\mathbf{k},j)$ denote, respectively, the frequency and the normal coordinate of the phonon with the wave vector $\mathbf{k}$ and the polarization j $(=\mathrm{L},\mathrm{T}_1,\mathrm{T}_2)$. We note that hereafter the vector $\mathbf{k}$ is restricted to the first Brillouin zone (FBZ) in contrast to the vector $\mathbf{q}$ which denotes a general wave vector. The displacement of the lth atom $\mathbf{u}(l)$ is expressed as

$$\mathbf{u}(l)=(NM)^{-1/2}\sum_{\mathbf{k},j}\mathbf{e}(\mathbf{k},j)Q(\mathbf{k},j)\exp[i\mathbf{k}\cdot\mathbf{R}(l)]\ , \tag{5}$$

where $\mathbf{e}(\mathbf{k},j)$ is the polarization vector and $\mathbf{R}(l)$ denotes the equilibrium position of the lth atom, expressed in terms of the fundamental translation vector as

$$\mathbf{R}(l)=\sum_{i=1}^{3} l_i\mathbf{a}_i\ . \tag{6}$$

As the Hamiltonian of the impurity we take

$$\begin{aligned}H_I&=M_IV_I^2/2+\sum_l v[\,|\,\mathbf{R}_I-\mathbf{R}(l)-\mathbf{u}(l)\,|\,]\\&\simeq M_IV_I^2/2+\sum_l v(\,|\,\mathbf{R}_I-\mathbf{R}(l)\,|\,)+\sum_l \mathbf{u}(l)\mathbf{u}(1)\cdot\mathbf{f}(\mathbf{R}_I,1)\ ,\end{aligned} \tag{7}$$

where $\mathbf{V}_I(\mathbf{R}_I)$ denotes velocity (position) of the impurity and $v(r)$ is the interaction between the impurity and a host-lattice atom. Assuming that each lattice atom performs small-amplitude oscillations around its equilibrium point, we retain in Eq. (7) terms up to linear in $\mathbf{u}(l)$, where

$$\mathbf{f}(\mathbf{R}_I,l)=-\nabla_{\mathbf{R}_I}v[\,|\,\mathbf{R}_I-\mathbf{R}(l)\,|\,] \tag{8}$$

represents the force on the impurity from the lth atom at its equilibrium position. With use of Eq. (5) and the Fourier transform as defined by

$$\tilde{v}(q)=\int d\mathbf{r}v(r)e^{i\mathbf{q}\cdot\mathbf{r}}\ , \tag{9}$$

we rewrite Eq. (7) as

$$\begin{aligned}H_I&=M_IV_I^2/2+n\sum_{\mathbf{G}_0}\tilde{v}(G_0)e^{-i\mathbf{G}_0\cdot\mathbf{R}_I}\\&\quad+\sum_{\mathbf{k},j}Q(\mathbf{k},j)F(\mathbf{R}_I;\mathbf{k},j)\ ,\end{aligned} \tag{10}$$

where

$$\begin{aligned}F(\mathbf{R}_I;\mathbf{k},j)=ni(NM)^{-1/2}&\sum_{\mathbf{G}_0}\mathbf{e}(\mathbf{k},j)\cdot(-\mathbf{k}+\mathbf{G}_0)\\&\times\tilde{v}(\,|\,-\mathbf{k}+\mathbf{G}_0\,|\,)e^{i(\mathbf{k}-\mathbf{G}_0)\cdot\mathbf{R}_I}\end{aligned} \tag{11}$$

and n $(=N/V)$ is the density of the host lattice. In deriving Eq. (11) use has been made of the relation

$$\sum_l\exp[i\mathbf{q}\cdot\mathbf{R}(l)]=N\sum_{\mathbf{G}_0}\delta_{\mathbf{q},\mathbf{G}_0}\quad(\mathbf{G}_0\in\mathrm{RLV})\ . \tag{12}$$

It is remarked that $\mathbf{G}_0$ denotes a general reciprocal-lattice vector (RLV) including the zero vector whereas $\mathbf{G}$ will be specifically used for nonzero RLV. From Eq. (11) we readily see the relation

$$F(\mathbf{R}_I;\mathbf{k},j)=F^*(\mathbf{R}_I;-\mathbf{k},j)\ . \tag{13}$$

III. GENERALIZED LANGEVIN EQUATION

For a set of dynamical variables $\mathbf{A}$, the following Langevin equation holds:[10]

$$\dot{\mathbf{A}}(t)=i\hat{\omega}\cdot\mathbf{A}(t)-\int_0^t ds\hat{\phi}(t-s)\cdot\mathbf{A}(s)+\mathbf{F}(t)\ . \tag{14}$$

Based on a physical picture that the impurity moves interacting with phonons in a periodic potential produced by the host crystalline solid, we take as $\mathbf{A}$

$$\mathbf{A}=\begin{bmatrix}\mathbf{P}_I\\ \exp(i\mathbf{G}\cdot\mathbf{R}_I)-\gamma(\mathbf{G})\end{bmatrix}\equiv\begin{bmatrix}\mathbf{P}_I\\ A_{\mathbf{G}}\end{bmatrix}\ , \tag{15}$$

where $\mathbf{G}$ denotes a set of nonzero RLV's with $\gamma(\mathbf{G})=\langle\exp(i\mathbf{G}\cdot\mathbf{R}_I)\rangle$ and $\mathbf{A}$ is a $(3+\infty)$-dimensional vector.[12] Some comments would be appropriate here as to the choice of the variables, Eq. (15). First, we are mainly interested in the Langevin equation for $\mathbf{P}_I(=M_I\mathbf{V}_I)$ and $A_{\mathbf{G}}$ included in $\mathbf{A}$ serves to extract coupling of the impurity to the periodic array of lattice atoms. In this sense our approach is similar to the mode-coupling theory,[13] where the bilinear variables $f(\mathbf{q})f(\mathbf{k}-\mathbf{q})$ are included in A only to obtain a nonlinear kinetic equation for the mode $f(\mathbf{k})$. Secondly, since higher powers of $\mathbf{P}_I$ are not included in $\mathbf{A}$ the resulting Langevin equation [(30)] is linear in $\mathbf{P}_I$ and from this linearity (in $\mathbf{P}_I$), the choice of the variables, (15), might be best suited to the case of small fluctuations in a momentum space or strong coupling (large friction) between the impurity and the host lattice. However, as we take full account of non-Markovian property of the Langevin equation (Secs. IV C and IV D), which includes effects from higher powers of $\mathbf{P}_I$,[10] we expect that our Langevin method can be used in the full range of the coupling strength.

To make the average of $\mathbf{A}$ vanish we subtract $\gamma(\mathbf{G})$ from $\exp(i\mathbf{G}\cdot\mathbf{R}_I)$. Since $\gamma(\mathbf{G})$ is an important quantity for subsequent analysis, we first consider $\gamma(\mathbf{G})$ based on the definition

$$\begin{aligned}\gamma(\mathbf{G})=c\int d\mathbf{P}_I\int d\mathbf{R}_I\left[\prod_{\mathbf{k},j}\int dP(\mathbf{k},j)\int dQ(\mathbf{k},j)\right]\\\times e^{-\beta(H_L+H_I)+i\mathbf{G}\cdot\mathbf{R}_I}\quad(\beta=1/k_BT)\ ,\end{aligned} \tag{16}$$

where the normalization constant c (and c' below) are specified from the obvious condition $\gamma(\mathbf{0})=1$. From Eqs. (4), (10), and (13) it follows that

$$\begin{aligned}\gamma(\mathbf{G})=c'\int d\mathbf{R}_I\exp\Bigg[&i\mathbf{G}\cdot\mathbf{R}_I-\beta n\sum_{\mathbf{G}'}\tilde{v}(G')e^{-i\mathbf{G}'\cdot\mathbf{R}_I}\\&+\beta\sum_{\mathbf{k},j}|\,F(\mathbf{R}_I;\mathbf{k},j)\,|^2[1/2\omega^2(\mathbf{k},j)]\Bigg]\ .\end{aligned} \tag{17}$$

Since the integrand in Eq. (17) is too complicated to obtain a closed expression for $\gamma(\mathbf{G})$, thus making subsequent analysis a difficult task, we hereafter assume that the interaction $v(r)$ between the impurity and the host-lattice atom is weak compared to the interaction among the host-lattice atoms. This is implied in the Hamiltonian (7) where each lattice atom was assumed to be tightly bound to its equilibrium position. Thus, our task in this section is to calculate $\gamma(\mathbf{G})$, $i\hat{\omega}$, and $\hat{\phi}(t)$ to order v^2. For the lattice with the inversion symmetry we obtain with use of Eq. (11),

$$\gamma(\mathbf{G})=-\beta n\tilde{v}(G)+(\beta^2 n^2/2)\sum_{\mathbf{G}'(\neq\mathbf{G})}\tilde{v}(G')\tilde{v}(|\mathbf{G}-\mathbf{G}'|)+[\beta n^2/(NM)]\sum_{\mathbf{G}_0,\mathbf{k},j}H(\mathbf{k},j\,|\,\mathbf{G}_0,\mathbf{G}_0+\mathbf{G})=\gamma(-\mathbf{G}), \tag{18}$$

where

$$H(\mathbf{k},j\,|\,\mathbf{G}_0,\mathbf{G}_0')=\tilde{v}(|\mathbf{k}+\mathbf{G}_0|)\tilde{v}(|\mathbf{k}+\mathbf{G}_0'|)\times\mathbf{e}(\mathbf{k},j)\cdot(\mathbf{k}+\mathbf{G}_0)\times\mathbf{e}(\mathbf{k},j)\cdot(\mathbf{k}+\mathbf{G}_0')/[2\omega^2(\mathbf{k},j)]\ . \tag{19}$$

A. The frequency matrix $i\hat{\omega}$

The frequency matrix is defined by[10]

$$i\hat{\omega}=(\dot{\mathbf{A}},\mathbf{A})(\mathbf{A},\mathbf{A})^{-1} \tag{20}$$

with

$$\dot{\mathbf{A}}=\begin{bmatrix}\dot{P}_I\\ \dot{A}_{\mathbf{G}}\end{bmatrix}=\begin{bmatrix}ni\sum_{\mathbf{G}}\mathbf{G}\cdot\tilde{v}(G)e^{i\mathbf{G}\cdot\mathbf{R}_I}-\sum_{\mathbf{k},j}Q(\mathbf{k},j)\nabla_{\mathbf{R}_I}F(\mathbf{R}_I;\mathbf{k},j)\\ i\mathbf{G}\cdot\mathbf{P}_I e^{i\mathbf{G}\cdot\mathbf{R}_I}/M_I\end{bmatrix} \tag{21}$$

and the innerproduct (f,g) of two arbitrary dynamical variables f and g is defined by $\langle fg^*\rangle$. Since $\langle\dot{f}g\rangle=-\langle f\dot{g}\rangle$, we see that

$$(\dot{\mathbf{A}},\mathbf{A})=ik_BT\begin{bmatrix}\hat{0}_{3\times3} & \mathbf{G}'\gamma(\mathbf{G}')\\ \mathbf{G}\gamma(\mathbf{G}) & \hat{0}_{\infty\times\infty}\end{bmatrix},\quad(\mathbf{A},\mathbf{A})=\begin{bmatrix}M_Ik_BT\hat{I}_3 & \hat{0}_{3\times\infty}\\ \hat{0}_{\infty\times3} & \alpha(\mathbf{G},\mathbf{G}')\end{bmatrix}, \tag{22}$$

where $\hat{0}_{3\times3}$, $\hat{0}_{\infty\times\infty}$, $\hat{0}_{3\times\infty}$, and $\hat{0}_{\infty\times3}$ are the zero matrices with sizes 3×3, $\infty\times\infty$, $3\times\infty$, and $\infty\times3$, respectively, and $\hat{I}_3$ denotes a 3×3 unit matrix. The matrix $\alpha(\mathbf{G},\mathbf{G}')=(A_{\mathbf{G}},A_{\mathbf{G}'})$ is given by

$$\alpha(\mathbf{G},\mathbf{G}')=\gamma(\mathbf{G}-\mathbf{G}')-\gamma(\mathbf{G})\gamma(\mathbf{G}')\ . \tag{23}$$

The inverse is easily obtained as

$$\alpha^{-1}(\mathbf{G},\mathbf{G}')=\delta_{\mathbf{G},\mathbf{G}'}+\beta n\tilde{v}(|\mathbf{G}-\mathbf{G}'|)(1-\delta_{\mathbf{G}\mathbf{G}'})+o(v^2)\ , \tag{24}$$

where the term of order v^2 is not necessary for the calculations below. From Eqs. (20), (22), and (24) we obtain, after some algebra,

$$(i\hat{\omega}\cdot\mathbf{A})_{\mathbf{P}_I}=-in\sum_{\mathbf{G}}\mathbf{G}\left[\tilde{v}(G)-(n/NM)\times\sum_{\mathbf{G}_0,\mathbf{k},j}H(\mathbf{k},j\,|\,\mathbf{G}_0,\mathbf{G}_0+\mathbf{G})\right]A_{\mathbf{G}}\ , \tag{25a}$$

$$(i\hat{\omega}\cdot\mathbf{A})_{A_{\mathbf{G}}}=i\mathbf{G}\cdot\mathbf{P}_I\gamma(\mathbf{G})/M_I\ , \tag{25b}$$

where the subscript $\mathbf{P}_I$ on $i\hat{\omega}\cdot\mathbf{A}$ of Eq. (25a) denotes the upper three components of $i\hat{\omega}\cdot\mathbf{A}$ and the subscript $A_{\mathbf{G}}$ has a similar meaning. We note from Eq. (18) that $A_{\mathbf{G}}$ in Eq. (25a) can be replaced by $\exp(i\mathbf{G}\cdot\mathbf{R}_I)$. As is shown in Appendix A it holds that

$$(i\hat{\omega}\cdot\mathbf{A})_{\mathbf{P}_I}=\langle\dot{\mathbf{P}}_I\rangle_{\mathbf{R}_I}=-\nabla_{\mathbf{R}_I}V_P(\mathbf{R}_I)\ , \tag{26}$$

where the last equality defines the periodic potential $V_p(\mathbf{R}_I)$. Thus the systematic force $(i\hat{\omega}\cdot\mathbf{A})_{\mathbf{P}_I}$ exerted on the impurity turns out to be the average force with the impurity *fixed* at position $\mathbf{R}_I$.

B. The friction kernel $\hat{\phi}(t)$

The random force $\mathbf{F}(t)$ in Eq. (14)is given by[10]

$$\mathbf{F}=\dot{\mathbf{A}}-i\hat{\omega}\cdot\mathbf{A}=\begin{bmatrix}\mathbf{F}_{\mathbf{P}_I}\\ F_{\mathbf{G}}\end{bmatrix}\ . \tag{27}$$

Since $\hat{\phi}(t)=(\mathbf{F}(t),\mathbf{F})(\mathbf{A},\mathbf{A})^{-1}$,[10] we see from Eqs. (22) and (24),

$$[\hat{\phi}(t-s)\cdot\mathbf{A}(s)]_{\mathbf{P}_I}=(M_I k_B T)^{-1}(\mathbf{F}_{\mathbf{P}_I}(t-s),\mathbf{F}_{\mathbf{P}_I})\cdot\mathbf{P}_I(s)+\sum_{\mathbf{G}}(\mathbf{F}_{\mathbf{P}_I}(t-s),F_{\mathbf{G}})A_{\mathbf{G}}\equiv\hat{\phi}_{\mathbf{P}_I}(t-s)\cdot\mathbf{P}_I(s)+\sum_{\mathbf{G}}\phi_{\mathbf{G}}(t-s)A_{\mathbf{G}}(s)\cdot \tag{28}$$

The first term on the right-hand side (rhs) of Eq. (28) represents damping effects on impurity motion due to *dynamic* coupling to phonons, while the second term represents a retarded periodic force of the form

$$-2\sum_{\mathbf{G}}\int_0^t ds\,\psi_{\mathbf{G}}(t-s)\sin[\mathbf{G}\cdot\mathbf{R}_I(s)]\ ,$$

where $\phi_{\mathbf{G}}(t)=i\psi_{\mathbf{G}}(t)$ is pure imaginary and of order v^2. [See Appendix B for detailed discussions on $\hat{\phi}(t)$]. Since the periodic force, Eq. (26), contains the dominant contribution of order v, we neglect in this paper the second term and will discuss effects of the retardation in the potential on impurity diffusion elsewhere for the case of nonweak interaction $v(r)$. In Appendix B we show that to order v^2,

$$\hat{\phi}_{\mathbf{P}_I}(t)=(M_I k_B T)^{-1}\sum_{\mathbf{k},j}\langle Q_0(\mathbf{k},j,t)Q_0(-\mathbf{k},j)\rangle_0\times\langle\nabla_{\mathbf{R}_{I,0}(t)}F(\mathbf{R}_{I,0}(t);\mathbf{k},j)\times\nabla_{\mathbf{R}_I}F(\mathbf{R}_I;\mathbf{k},j)\rangle_0\ , \tag{29}$$

where the time evolution of $Q_0(\mathbf{k},j)$ and $\mathbf{R}_{I,0}(t)$ in Eq. (29) is governed by the Hamiltonian $H_0=H_L+M_I V_I^2/2$ and the average $\langle\cdots\rangle_0$ is over the canonical distribution $z_0\exp(-\beta H_0)$.

Summing up the results in this section, we divide the force $\dot{\mathbf{P}}_I$ on the impurity into the periodic force due to the static coupling to the host lattice and the random force $\mathbf{F}_{\mathbf{P}_I}(t)$, Eq. (27), which gives rise to damping effects through the FDT, Eq. (29). The generalized Langevin equation for $\mathbf{P}_I$ is from Eqs. (14), (26), and (28):

$$d\mathbf{P}_I(t)/dt=-\nabla_{\mathbf{R}_I(t)}V_p(\mathbf{R}_I(t))-\int_0^t ds\,\hat{\phi}_{\mathbf{P}_I}(t-s)\cdot\mathbf{P}_I(s)+\mathbf{F}_{\mathbf{P}_I}(t)\ . \tag{30}$$

IV. IMPURITY DIFFUSION IN THE DEBYE LATTICE

A. Debye model

The results obtained above for the periodic potential, Eqs. (25a) and (26), and the kernel, Eq. (29), involve the details of phonon dynamics through $\omega(\mathbf{k},j)$ and $\mathbf{e}(\mathbf{k},j)$. We now calculate them explicitly for an isotropic Debye model,

$$\omega(\mathbf{k},j=\mathrm{L})=\omega_{\mathrm{L}}(k),\quad \omega(\mathbf{k},j=\mathrm{T}_1,\mathrm{T}_2)=c_{\mathrm{T}}k\ , \tag{31}$$

where $\omega_{\mathrm{L}}(k)=c_L k$ (c_L: is the longitudinal sound velocity) for an acoustic system and $\omega_{\mathrm{L}}(k)=\omega_p$ (the plasma frequency) for an optic one. For the latter we have in mind a one-component plasma (solid phase) or a simplified model of a superionic conductor with the charge of one ionic species smeared out to form a charge-neutralizing background. Assuming that $\mathbf{e}(\mathbf{k},\mathrm{L})$ is parallel to $\mathbf{k}$, we have[11]

$$\sum_{i=1}^{2}e_\alpha(\mathbf{k},\mathrm{T}_i)e_\beta(\mathbf{k},\mathrm{T}_i)=\delta_{\alpha\beta}-k_\alpha k_\beta/k^2\ . \tag{32}$$

From Eqs. (19), (31), and (32) we see

$$\sum_j H(\mathbf{k},j\mid\mathbf{G}_0,\mathbf{G}_0')=\tilde{v}(\mid\mathbf{k}+\mathbf{G}_0\mid)\tilde{v}(\mid\mathbf{k}+\mathbf{G}_0'\mid)\left[\frac{(\mathbf{k}+\mathbf{G}_0)\cdot(\mathbf{k}+\mathbf{G}_0')}{2\omega^2(k,\mathrm{T})}+\frac{\mathbf{k}\cdot(\mathbf{k}+\mathbf{G}_0)\mathbf{k}\cdot(\mathbf{k}+\mathbf{G}_0')}{2k^2}\left[\frac{1}{\omega^2(k,\mathrm{L})}-\frac{1}{\omega^2(k,\mathrm{T})}\right]\right] \tag{33}$$

and from Eqs. (25) and (26),

$$V_p(\mathbf{R}_I)=n\sum_{\mathbf{G}}\left[\tilde{v}(G)-(n/NM)\sum_{\mathbf{G}_0,\mathbf{k},j}H(\mathbf{k},j\mid\mathbf{G}_0,\mathbf{G}_0+\mathbf{G})\right]e^{i\mathbf{G}\cdot\mathbf{R}_I}\ . \tag{34}$$

Noting that $\mathbf{R}_{I,0}(t)=\mathbf{R}_I+(\mathbf{P}_I/M_I)t$ and from Eqs. (11), (32), and (B8) we obtain

$$\hat{\phi}_{\mathbf{P}_I}(t)=(n^2/MM_IN)\sum_{\mathbf{k},\mathbf{G}_0,\mathbf{G}_0'}\tilde{v}(\mid-\mathbf{k}+\mathbf{G}_0\mid)\tilde{v}(\mid\mathbf{k}+\mathbf{G}_0'\mid)\gamma(\mathbf{G}_0+\mathbf{G}_0')\langle e^{-it\mathbf{P}_I\cdot(\mathbf{G}_0-\mathbf{k})/M_I}\rangle_0(\mathbf{k}-\mathbf{G}_0)(\mathbf{k}+\mathbf{G}_0')\times\{(-\mathbf{k}+\mathbf{G}_0)\cdot(\mathbf{k}+\mathbf{G}_0')D_{\mathrm{T}}(k,t)+\mathbf{k}\cdot(-\mathbf{k}+\mathbf{G}_0)\mathbf{k}\cdot(\mathbf{k}+\mathbf{G}_0')/k^2[D_{\mathrm{L}}(k,t)-D_{\mathrm{T}}(k,t)]\} \tag{35}$$

with $D_i(k,t)=\cos[\omega(k,i)t]/\omega^2(k,i)$ ($i=\mathrm{L},\mathrm{T}$). Since $\gamma(\mathbf{G}_0)$ is of order v except for $\gamma(\mathbf{0})=1$ and from

$$\langle e^{i\mathbf{P}_I\cdot\mathbf{q}t/M_I}\rangle_0=e^{-(k_BT/2M_I)q^2t^2}\equiv\psi_{s,0}(q,t)\ , \tag{36}$$

$\hat{\phi}_{\mathbf{P}_I}(t)$ is further simplified as

$$\hat{\phi}_{\mathbf{P}_I}(t)=(n^2/MM_IN)\sum_{\mathbf{k},\mathbf{G}_0}[\tilde{v}(|-\mathbf{k}+\mathbf{G}_0|)]^2\psi_{s,0}(|\mathbf{G}_0-\mathbf{k}|,t)(\mathbf{k}-\mathbf{G}_0)(\mathbf{k}-\mathbf{G}_0)$$
$$\times\{(\mathbf{k}-\mathbf{G}_0)^2D_{\mathrm{T}}(k,t)+[\mathbf{k}\cdot(\mathbf{k}-\mathbf{G}_0)]^2/k^2[D_{\mathrm{L}}(k,t)-D_{\mathrm{T}}(k,t)]\}\ , \tag{37}$$

where $\psi_{s,0}(k,t)$ denotes the self-correlation function of the ideal gas.[14]

B. Gaussian interaction

In order to evaluate the $V_p(\mathbf{R}_I)$ and $\hat{\phi}_{\mathbf{P}_I}(t)$ explicitly we now specify $v(r)$ to be the Gaussian repulsive interaction

$$v(r)=V_0\exp(-r^2/\sigma^2)\ , \tag{38}$$

where σ measures the range of the interaction and

$$\tilde{v}(q)=2^{-1}\pi^{3/2}V_0\sigma^3\exp(-\sigma^2q^2/4)\ . \tag{39}$$

Let us assume that σ satisfies the condition

$$\sigma^2G_1^2/4\simeq(\sigma/a)^2\pi^2>1\ , \tag{40}$$

where $G_1\simeq 2\pi/a$ denotes the magnitude of the smallest (nonzero) RLV with a, a lattice constant. If we take a simple cubic host lattice for simplicity and retain, based on Eq. (40), the contribution from the smallest possible RLV in the sums over $\mathbf{G}$ and $\mathbf{G}_0$ appearing in Eqs. (34) and (37), we obtain for $V_p(\mathbf{R}_I)$

$$V_p(\mathbf{R}_I)=U[\cos(2\pi X_I/a)+\cos(2\pi Y_I(a)+\cos(2\pi Z_I/a)]\ , \tag{41}$$

where $\mathbf{R}_I=(X_I,Y_I,Z_I)$ and

$$U=2n\tilde{v}(2\pi/a)-(n^2/NM)\sum_{\mathbf{k}}\tilde{v}(k)[\tilde{v}(|\mathbf{k}+(2\pi/a)\mathbf{i}|)\mathbf{k}\cdot(\mathbf{k}+(2\pi/a)\mathbf{i})+\tilde{v}(|\mathbf{k}-(2\pi/a)\mathbf{i}|)\mathbf{k}\cdot(\mathbf{k}-(2\pi/a)\mathbf{i})]/\omega^2(k,\mathrm{L}) \tag{42}$$

with $\mathbf{i}$ denoting the unit vector (1,0,0) in the reciprocal-lattice space. For the kernel it follows similarly as

$$\hat{\phi}_{\mathbf{P}_I}(t)=(n^2/3MM_IN)\sum_{\mathbf{k}}[v(k)]^2\psi_{s,0}(k,t)k^4D_{\mathrm{L}}(k,t)\hat{I}\ . \tag{43}$$

From Eqs. (41) and (43) we see that the three components of the Langevin equation (30) decouple, yielding precisely the one-dimensional form given by Eq. (1).

It is interesting to note that both $V_p(\mathbf{R}_I)$ and the memory function $K(t)$ (together with the retarded potential, see Appendix B) are independent of the transverse phonon modes. We showed above from a perturbation theory that density fluctuations of the host lattice or longitudinal phonon modes are of crucial importance in impurity diffusion in solids.

Equation (42) for the amplitude U is transformed to

$$U=U_1\left[1-(\sigma V_0/2M\pi^{1/2})\int_0^{k_{\max}}dk\,[k^2/\omega^2(k,\mathrm{L})]e^{-\sigma^2k^2/2}[(1+\sigma^2k^2/2)(\sinh S)/S-\cosh S]\right]\ , \tag{44}$$

where $S=\sigma^2\pi k/a$,

$$U_1=\pi^{3/2}V_0(\sigma/a)^3e^{-(\sigma/a)^2\pi^2} \tag{45}$$

and $k_{\max}$ denotes the radius of the spherical FBZ, $ak_{\max}=(6\pi^2)^{1/3}$. From the condition (40) we can replace the upper limit $k_{\max}$ in the integral in Eq. (44) by infinity. Although we retain only the dominant part U_1 of U, Eq. (44) is used to estimate the magnitude of the term of order v^2.

The function $K(t)$ is from Eq. (43)

$$K(t)=(n\pi V_0^2\sigma^6/24MM_I)\times\int_0^{k_{\max}}dk\,k^6D_{\mathrm{L}}(k,t)e^{-k^2[\sigma^2/2+k_BTt^2/2M_I]}\ . \tag{46}$$

Since the integrand in Eq. (46) decays to zero rapidly from the condition (40) as k becomes large, we set $k_{\max}$ infinity without appreciable errors to obtain

$$K_A(t)=(\sqrt{\pi}B/8c_L^2)e^{-c_L^2t^2/4\tau}\times(3\tau^{-5/2}-3c_L^2t^2\tau^{-7/2}+c_L^4t^4\tau^{-9/2}/4)\ , \tag{47}$$

$$K_O(t)=(15\sqrt{\pi}B/16\omega_p^2)\tau^{-7/2}\cos(\omega_pt)\ , \tag{48}$$

where the subscripts A and O refer to the acoustic and optic systems, respectively, and

$$B=\pi nV_0^2\sigma^6/(24MM_I)\ , \tag{49}$$

$$\tau=(\sigma^2+k_BTt^2/M_I)/2\ . \tag{50}$$

Asymptotically $K(t)$ behaves as $K_A(t)\sim t^{-5}$ and $K_O(t)\sim t^{-7}$.

C. The memory function $K(t)$

As an order-of-magnitude example we choose the following values for a (the lattice constant), M (mass of the

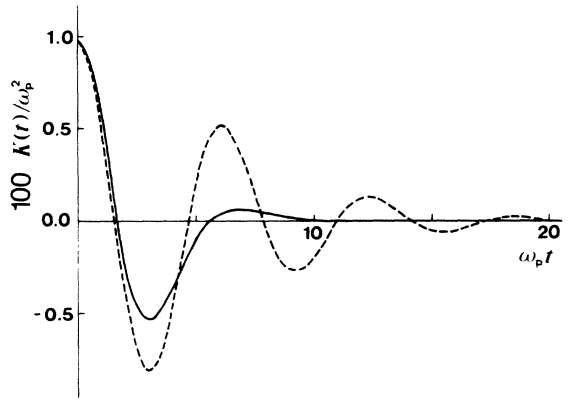

FIG. 1. Memory function $K(t)$ for $\gamma \equiv M_I/M = \frac{1}{3}$. The solid and dashed curves represent $K_A(t)$ and $K_0(t)$, respectively, for $T = 100$ K. Other values of parameters characterizing our system are given in Eq. (51) and this is the same for Fig. 2.

host-lattice atom), σ and V_O [Eq. (38)], and c_L and ω_p [Eq. (31)]:

$$\begin{aligned} &a = 3\times 10^{-8} \text{ cm}, \quad \sigma = a/\sqrt{3}, \quad c_L = 10^5 \text{ cm/sec} , \\ &\omega_p = c_L k_{\max} = 1.3\times 10^{13}/\text{sec} , \\ &V_0 = (5\times 10^3 \text{ K}) k_B = 6.9\times 10^{-13} \text{ erg} , \\ &M = 100 \text{ amu} = 1.66\times 10^{-22} \text{ g} . \end{aligned} \tag{51}$$

The value of V_0 in Eq. (51) came from the following consideration. If we assume that the interaction between the lattice atoms is given by Eq. (38) with V_0 replaced by V_L, the V_L is estimated, from the relation $d^2v(r)/dr^2 (r=a) = Mc_L^2/a^2$ and Eq. (51), to be $V_L = (10^4 \text{ K}) k_B$, leading to our choice $V_0 = V_L/2 = (5\times 10^3 \text{ K}) k_B$.

In Figs. 1 and 2 we show the memory function $K(t)$ for the case $\gamma = M_I/M = \frac{1}{3}$ and $\gamma = 3$, respectively. We note that $K_O(t)$ exhibits an oscillatory behavior for long time compared with $K_A(t)$, which decays to zero rapidly after one overdamped oscillation. This feature of $K_O(t)$ becomes more and more conspicuous as temperature becomes low and the ratio γ becomes large. This is consistent with a physical picture that a heavy impurity, which moves slowly in the lattice, feels more or less coherent "random" force through interaction with optic phonon modes. The rapid decay of $K_A(t)$ results mainly from the relation $\omega(k,\mathrm{L}) = c_L k$, Eq. (31).

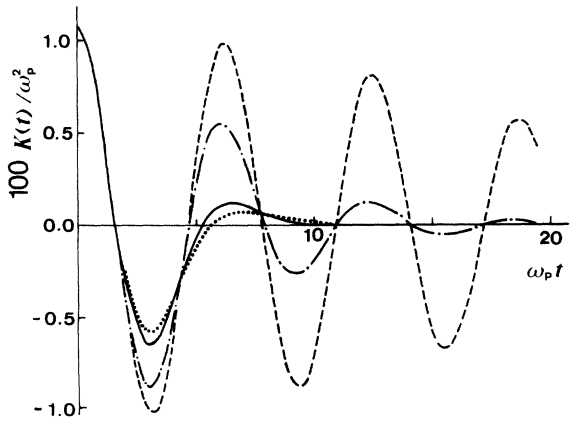

FIG. 2. Memory function $K(t)$ for $\gamma = 3$. The solid and dotted curves represent $K_A(t)$ for $T = 100$ and 1000 K, respectively. Dashed and dash-dotted curves represent $K_0(t)$ for $T = 100$ and 1000 K, respectively.

D. Diffusion constant

We first consider the acoustic case and calculate the diffusion constant D under the Markovian approximation

$$K_A(t) = 2\zeta\delta(t), \quad \zeta \equiv \int_0^\infty dt K_A(t) , \tag{52}$$

where ζ denotes the friction constant. We note from Eq. (52) that Eq. (30) reduces precisely to the form assumed by Fulde *et al.*, Eqs. (1)–(3).[7] The approximation (52) is based on the observation that the decay time of $K_A(t)$ is of the order of the period of the phonon with the largest frequency. The constant is obtained from Eq. (43) as

$$\zeta = (\pi n V_0^2 \sigma^2/24 M c_L^2)(2\pi/k_B T M_I)^{1/2} e^{-M_I c_L^2/2k_B T} . \tag{53}$$

The important parameter which measures the strength of damping effects is $\bar{\zeta} = \zeta/\omega_0$, where ω_0 denotes the natural frequency of the impurity at the bottom of the sinusoidal potential (41),[15]

$$\omega_0^2 = (2\pi/a)^2 U_1/M_I . \tag{54}$$

We note that the correction to U_1 from the term of order v^2 is less than 10% of U_1 for the system specified by Eqs. (51). For the range of the values of T and γ we consider ($T < 1000$ K, $\gamma > 0.1$) the condition $\bar{\zeta} < 0.01$ is satisfied and we can employ the following Kramers formula[15,16] for the thermal activation rate Γ, valid for the underdamped case:

$$\Gamma = (\xi/k_B T)(4E_b/\pi) e^{-E_b/k_B T} , \tag{55}$$

where E_b ($= 2U_1$) is the height of the barrier $V_p(\mathbf{R}_I)$. If we neglect effects of successive jumps, the diffusion constant D_A is given by

$$\begin{aligned} D_A = \Gamma a^2/2 &= (2\pi/k_B T M_I)^{1/2} (U_1 V_0^2 \sigma^2/6 a M c_L^2 k_B T) \\ &\times e^{-E_a/k_B T} , \end{aligned} \tag{56}$$

where we note that the activation energy $E_a = 2U_1 + M_I c_L^2/2$ has the contribution from dynamic coupling to the host lattice, $M_I c_L^2/2$, in addition to the one from static coupling, $2U_1$. Impurity-mass dependence of the prefactor, proportional to $M_I^{-1/2}$, is the same with the result from the transition-state theory.[5] As to the dependence of D_A on the velocity of sound we have

$$D_A \propto c_L^2 \exp(-M_I c_L^2/2k_B T) ,$$

showing that the impurity has difficulty in moving through the lattice as it becomes stiff due to strong coupling among the lattice atoms. A similar result was obtained by Kleppmann and Zeyher,[17] who showed with use of a mode-coupling approximation that the soft lattice (c_L small) leads to a small activation barrier. In Fig. 3 we show the general dependence of D_A on T and γ. Due to

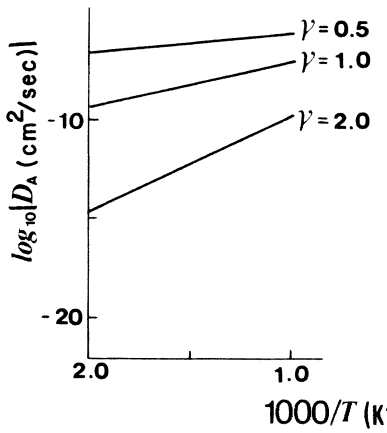

FIG. 3. Temperature and γ dependence of D_A (cm^2/sec) as calculated from Eqs. (56) and (51).

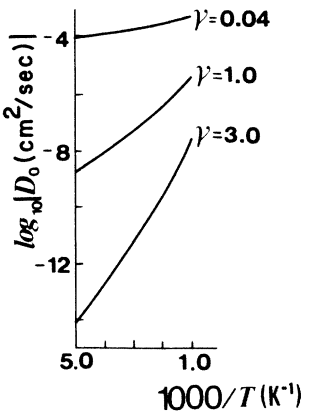

FIG. 4. Temperature and γ dependence of D_0 (cm^2/sec) as calculated from Eqs. (59), (51), and $D=\Gamma a^2/2$.

the factor $\exp(-M_I c_L^2/2k_BT)$ in Eq. (56), small γ results in large D_A.

Next we turn to the optic case. Since the kernel $K_O(t)$ oscillates for a long time in general, we cannot employ the Markovian approximation (52) as in the acoustic case. Recently, considerable attention has been paid to the activation rate of non-Markovian processes.[18–21] Carmeli and Nitzan derived from the non-Markovian Langevin equation, (1) and (2), the following Fokker-Planck equation for the action $J=(1/2\pi)\oint P\,dX$ in the underdamped case:[18]

$$\frac{\partial P(J,t)}{\partial t}=\frac{\partial}{\partial J}\left[\epsilon(J)\left[\omega(E)+k_BT\frac{\partial}{\partial J}\right]P(J,t)\right], \tag{57}$$

where $\omega(E)$ is the frequency given by $dJ/dE=1/\omega(E)$. The action-diffusion constant $\epsilon(J)$ is defined by[18,19]

$$\epsilon(J)=[M_I/\omega^2(E)]\int_0^\infty dtK_0(t)\langle V_I(t)V_I\rangle, \tag{58}$$

where the velocity-correlation function is defined for the deterministic motion with $\langle\cdots\rangle$ denoting the average over the initial phase ϕ_0 for a fixed action value J. From Eq. (57) it follows that[18]

$$\Gamma=\left[\int_0^{E_b}dEe^{E/k_BT}[k_BT\omega(E)\epsilon(J)]^{-1}\int_0^E dE'e^{-E'/k_BT}/\omega(E')\right]^{-1}\equiv\tau_r^{-1}, \tag{59}$$

where τ_r denotes the mean residence time of the impurity in the state $E<E_b$. As before, the constant D_0 is given by $D_0=\Gamma a^2/2$. For our sinusoidal potential it holds that[19]

$$\begin{aligned}&\omega(E)=\omega_0\pi[2K(e)]^{-1},\\&J(E)=(4E_b/\pi\omega_0)[E(e)-(1-e)K(e)]\quad(e\equiv E/E_b),\end{aligned} \tag{60}$$

where $K(e)$ and $E(e)$ are the complete elliptic integrals of the first and second kind, respectively,[22] and to a good approximation[19]

$$\epsilon(J)=[J/\omega(E)]\int_0^\infty dtK_0(t)\cos[\omega(E)t]. \tag{61}$$

For the kernel, Eq. (48), we obtain

$$\begin{aligned}\epsilon(J)=w\{&|\omega(E)-\omega_p|^3K_3[(\sigma^2M_I/k_BT)^{1/2}|\omega(E)-\omega_p|]\\&+(\omega_p\to-\omega_p)\},\end{aligned} \tag{62}$$

where

$$w=15\pi BJM_I^2/[16\sqrt{2}\Gamma(\tfrac{7}{2})\omega(E)\omega_p^2\sigma^3(k_BT)^2] \tag{63}$$

with B given by Eq. (49) and $\Gamma(x)$ and $K_3(x)$ denote the Gamma function and the modified Bessel function of the third order, respectively.[22]

Figure 4 shows the impurity-mass dependence of D_0 calculated from Eqs. (59) and (62). We observe the sharp increase of D_0 as γ becomes small. The origin of this behavior is traced mainly to the γ dependence of the action (or energy) diffusion constant $\epsilon(J)$. As γ becomes small (a light impurity), the natural frequency ω_0 and consequently $\omega(E)$, Eq. (60), become large and comparable with ω_p ($=1.3\times10^{13}$/sec) near $\gamma=0.04$. Since $K_3(x)$ decreases exponentially for large x,[22] we have a large $\epsilon(J)$ for small γ values, leading to the large hopping rate Γ from Eq. (59). Expressed in a qualitative way, the diffusion constant becomes large if the frequency Ω of the random force, which characterizes the oscillatory behavior of the kernel $K_O(t)$ and in our case $\Omega=\omega_p$, is near the natural frequency ω_0 and the action diffusion constant becomes large according to Eq. (61). This may be considered as a kind of resonance and a similar problem is studied based on a simple stochastic model in Ref. 21.

V. SOME REMARKS

In this paper we studied impurity diffusion in solids, based on a simple Hamiltonian model and the exact Langevin theory.[10] Our approach is first to obtain stochastic (kinetic) description for impurity (defect) dynamics and then to study the resulting Langevin equation. Al-

though the approach seems to be quite general and able to cope with both many-body and nonlinear effects in a systematic way, some problems to be stated below are left untouched and these need some elaborations.

First, effects of successive jumps,[23] which may be important at low temperature, are neglected in our calculation of the diffusion constant. In order to include the effects, we should start from the well-known microscopic expression for D,[14]

$$D=\int_0^\infty dt\langle V_I(t)V_I\rangle \ . \tag{64}$$

So far as we know, the velocity autocorrelation function (VAF) for non-Markovian processes as governed by Eq. (1) or (30) has not been studied in detail.[24] Secondly, our theory is limited to atomic diffusion via interstitial mechanism in contrast with the TST (Refs. 5 and 25) and the DT (Ref. 6). In this respect we consider that a soliton picture[26] might be useful in dealing with diffusion via vacancy mechanism. Thirdly we chose a rather simple model, e.g., a harmonic lattice, weak interaction $v(r)$, and a one-component host lattice in which acoustic and optic phonons are not coexistent. This is mainly to present our approach in a transparent form, preventing a series of approximations necessary to deal with more realistic system from obscuring the structure of our theory.

Finally we comment on our recent work[9] which investigates diffusion in liquids and solids based on a linear-response method. In Ref. 9 we gave the following expressions for the potential and the kernel:

$$V_p(\mathbf{R}_I)=n\sum_{\mathbf{G}}\tilde{v}(G)e^{-W(G)+i\mathbf{G}\cdot\mathbf{R}_I} \ , \tag{65}$$

$$K(t)=n^2/(3MM_INk_BT)\sum_{\mathbf{k}}[\tilde{v}(k)]^2e^{-2W(k)}k^4 \times\langle Q(\mathbf{k},\mathrm{L},t)Q(-\mathbf{k},\mathrm{L})\rangle\psi_s(k,t), \tag{66}$$

where $W(k)$ denotes the Debye-Waller factor, $W(k)=k^2\langle u^2\rangle/6$, and $\psi_s(k,t)$ and $\langle Q(\mathbf{k},\mathrm{L},t)Q(-\mathbf{k},\mathrm{L})\rangle$ are the self-correlation function of the impurity and the phonon-correlation function, respectively. Noting that Eq. (43) for $K(t)$ is rewritten from Eq. (B8) as

$$K(t)=n^2/(3MM_INk_BT) \times\sum_{\mathbf{k}}[v(k)]^2k^4\langle Q(\mathbf{k},\mathrm{L},t)Q(-\mathbf{k},\mathrm{L})\rangle_0\psi_{s,0}(k,t), \tag{67}$$

we see that if $W(k)$ is set zero and $\langle Q(\mathbf{k},\mathrm{L},t)Q(-\mathbf{k},\mathrm{L})\rangle$ and $\psi_s(k,t)$ in Eq. (66) are replaced by their noninteracting $[v(r)=0]$ limits, Eqs. (65) and (66) are reduced to the perturbation results, Eqs. (34) and (67).

APPENDIX A: DERIVATION OF EQ. (26)

In order to interpret Eq. (25a) physically, let us rewrite it in a real-space form. With use of the Poisson sum formula

$$\sum_{\mathbf{G}_0}e^{i\mathbf{G}_0\cdot\mathbf{R}_I}=\sum_l\delta(\mathbf{R}_I-\mathbf{R}(l)) \tag{A1}$$

and Eq. (9) the first term on the rhs of Eq. (25a) is expressed as $-\nabla_{\mathbf{R}_I}\sum_l v(|\mathbf{R}_I-\mathbf{R}(l)|)$, representing the periodic potential produced by the host-lattice atoms at their equilibrium positions. Introducing the static displacement-correlation function of the harmonic lattice by[11]

$$G_{\alpha\beta}(\mathbf{R}(l))=\langle u_\alpha(\mathbf{R}(l))u_\beta(\mathbf{o})\rangle=(k_BT/NM)\sum_{\mathbf{k},j}e_\alpha(\mathbf{k},j)e_\beta(\mathbf{k},j)e^{i\mathbf{k}\cdot\mathbf{R}(l)}/\omega^2(\mathbf{k},j) \tag{A2}$$

with α and β denoting the Cartesian components, the second term on the rhs of Eq. (25a) is expressed from Eq. (19) as

$$-\nabla_{\mathbf{R}_I}\left[-(2k_BT)^{-1}\sum_{\substack{\alpha,\beta,\\ l,l'}}\frac{\partial v(|\mathbf{R}_I-\mathbf{R}(l)|)}{\partial R_{I,\alpha}}G_{\alpha\beta}(\mathbf{R}(l')-\mathbf{R}(l))\frac{\partial v(|\mathbf{R}_I-\mathbf{R}(l')|)}{\partial R_{I,\beta}}\right] . \tag{A3}$$

On the other hand, fixing the impurity at position $\mathbf{R}_I$, we calculate the average displacement $\langle\mathbf{u}(l)\rangle_{\mathbf{R}_I}$ to linear order in $v(r)$ to get

$$\langle u_\alpha(l)\rangle_{\mathbf{R}_I}\equiv\sum_{l',\beta}G_{\alpha\beta}(\mathbf{R}(l)-\mathbf{R}(l'))\frac{\partial v(|\mathbf{R}_I-\mathbf{R}(l')|)}{\partial R_{I,\beta}} \ . \tag{A4}$$

From Eqs. (A3), (A4), and (21) for $\dot{\mathbf{P}}_I$, we obtain Eq. (26).

APPENDIX B: TIME EVOLUTION AND THE MEMORY KERNEL

The random force $\mathbf{F}(t)$ in Eq. (14) evolves in time according to

$$\mathbf{F}(t)=\exp[(1-P)iLt]\mathbf{F}\equiv U(t)\mathbf{F} \ , \tag{B1}$$

where L is the Liouville operator of the system $H=H_L+H_I$ and P is the projection operator onto $\mathbf{A}$, Eq. (15). For perturbation calculations it is convenient to express iL, P, and the ensemble average $\langle\cdots\rangle$ in powers of v as follows:

$$iL=\left[(\mathbf{P}_I/M_I)\cdot\nabla_{\mathbf{R}_I}+\sum_{\mathbf{k},j}\left[\dot{Q}(\mathbf{k},j)\frac{\partial}{\partial Q(\mathbf{k},j)}-\omega^2(\mathbf{k},j)Q(\mathbf{k},j)\frac{\partial}{\partial\dot{Q}(\mathbf{k},j)}\right]\right]$$
$$+\left[-\nabla_{\mathbf{R}_I}H_I\cdot\nabla_{\mathbf{P}_I}-\sum_{\mathbf{k},j}F^*(\mathbf{R}_I;\mathbf{k},j)\frac{\partial}{\partial\dot{Q}(\mathbf{k},j)}\right]\equiv iL_0+iL_1\ , \tag{B2}$$

$$PB=\left[\langle B\mathbf{P}_I\rangle_0\cdot\mathbf{P}_I/M_Ik_BT+\sum_{\mathbf{G}}\langle Be^{-i\mathbf{G}\cdot\mathbf{R}_I}\rangle_0e^{i\mathbf{G}\cdot\mathbf{R}_I}\right]$$
$$+\left[\langle B\mathbf{P}_I\rangle_1\cdot\mathbf{P}_I/M_Ik_BT+\sum_{\mathbf{G}}\langle Be^{-i\mathbf{G}\cdot\mathbf{R}_I}\rangle_1e^{i\mathbf{G}\cdot\mathbf{R}_I}+\sum_{\mathbf{G},\mathbf{G}'}\langle Be^{-i\mathbf{G}\cdot\mathbf{R}_I}\rangle_0\beta n\tilde{v}(|\mathbf{G}-\mathbf{G}'|)e^{i\mathbf{G}'\cdot\mathbf{R}_I}\right]$$
$$\equiv P_0B+P_1+o(v^2)\ ,\langle\cdots\rangle=Z_0^{-1}\int d\Gamma e^{-\beta H_0}[\cdots]\left[1-\beta n\left[\sum_{\mathbf{G}}\tilde{v}(G)e^{i\mathbf{G}\cdot\mathbf{R}_I}+\sum_{\mathbf{k},j}Q(\mathbf{k},j)F(\mathbf{R}_I;\mathbf{k},j)\right]\right] \tag{B3}$$

$$\equiv\langle\cdots\rangle_0+\langle\cdots\rangle_1+o(v^2)\ . \tag{B4}$$

In Eq. (B3) we assumed $\langle B\rangle=0$ and H_0 in Eq. (B4) denotes $H_L+M_IV_I^2/2$. Since $\mathbf{F}_{\mathbf{P}_I}$, Eq. (27), is of order v the kernel $\hat{\phi}_{\mathbf{P}_I}(t)$ is written to order v^2 as

$$\hat{\phi}_{\mathbf{P}_I}(t)=\langle\mathbf{F}_{\mathbf{P}_I,0}(t)\mathbf{F}_{\mathbf{P}_I}\rangle_0/M_Ik_BT\ , \tag{B5}$$

where $\mathbf{F}_{\mathbf{P}_I,0}(t)=\exp[(1-P_0)iL_0t]=U_0(t)\mathbf{F}_{\mathbf{P}_I}$. For a dynamical variable linear in a phonon variable $Q(\mathbf{k},j)$, such as $\mathbf{F}_{\mathbf{P}_I}$, the projection operator P_0 in $U_0(t)$ is seen from Eqs. (B2), (B3), and the fact $\langle Q(\mathbf{k},j)\rangle_0=\langle\dot{Q}(\mathbf{k},j)\rangle_0=0$ to have no effects, leading to

$$U_0(t)\mathbf{F}_{\mathbf{P}_I}=\exp(iL_0t)\mathbf{F}_{\mathbf{P}_I}\ . \tag{B6}$$

Thus for a variable of the form $B=Q(\mathbf{k},j)g(\mathbf{R}_I,\mathbf{P}_I)$ it holds that

$$U_0(t)Q(\mathbf{k},j)g(\mathbf{R}_I,\mathbf{P}_I)=Q_0(\mathbf{k},j,t)g(\mathbf{R}_I+\mathbf{P}_It/M_I,\mathbf{P}_I)\ . \tag{B7}$$

In passing we note the relation[11]

$$\langle Q_0(\mathbf{k},j,t)Q(\mathbf{k}',j')\rangle_0=\delta_{\mathbf{k},-\mathbf{k}'}\delta_{j,j'}[k_BT/\omega^2(\mathbf{k},j)]\cos[\omega(\mathbf{k},j)t]\ , \tag{B8}$$

which is used to obtain Eq. (35) from Eq. (29).

Next we consider the kernel

$$\boldsymbol{\phi}_{\mathbf{G}}(t)=(\mathbf{F}_{\mathbf{P}_I}(t),F_{\mathbf{G}})=(\mathbf{F}_{\mathbf{P}_I},F_{\mathbf{G}}(-t))$$

(Ref. 10). With use of the expansion

$$U(-t)=U_0(-t)+\int_0^{-t}dsU_0(-t-s)[(1-P_0)iL_1-P_1iL_0]\times U_0(s)+o(v^2)\ , \tag{B9}$$

we obtain

$$F_{\mathbf{G}}(-t)=F_{\mathbf{G},0}(-t)+F_{\mathbf{G},1}(-t)+o(v^2) \tag{B10}$$

and consider first

$$F_{\mathbf{G},0}(-t)=U_0(-t)F_{\mathbf{G}}=\sum_{m=0}^{\infty}(-t)^m/m![(1-P_0)iL_0]^mF_{\mathbf{G}}\ . \tag{B11}$$

From Eqs. (B2) and (B3) we readily see that

$$[(1-P_0)iL_0]^mF_{\mathbf{G}}=f_m(\alpha_p)\exp(i\mathbf{G}\cdot\mathbf{R}_I)\quad(m>1)\ , \tag{B12}$$

where $\alpha_p=i\mathbf{G}\cdot\mathbf{P}_I/M_I$ and

$$f_m(\alpha_p)=\alpha_pf_{m-1}(\alpha_p)-\langle\alpha_pf_{m-1}(\alpha_p)\rangle_0\ . \tag{B13}$$

For $m=0$, $\exp(i\mathbf{G}\cdot\mathbf{R}_I)$ in Eq. (B12) should be replaced by $A_G=\exp(i\mathbf{G}\cdot\mathbf{R}_I)-\gamma(\mathbf{G})$. However we can use Eq. (B12) for $m=0$ since the constant $\gamma(\mathbf{G})$ does not contribute to $\boldsymbol{\phi}_{\mathbf{G}}(t)$. The polynomial $f_m(\alpha_p)$ is successively determined from Eq. (B13) with the initial condition $f_0(\alpha_p)=\alpha_p$.

From the fact that $\mathbf{F}_{\mathbf{P}_I}$ is independent of $\mathbf{P}_I$ and $\langle f_m(\alpha_p)\rangle_0=0$, $F_{\mathbf{G},0}(-t)$ in Eq. (B10) does not contribute to $\boldsymbol{\phi}_{\mathbf{G}}(t)$. Now we turn to $F_{\mathbf{G},1}(-t)$ which is expressed from Eqs. (B9), (B11), and (B12) as

$$F_{\mathbf{G},1}(-t)=\int_0^{-t}dsU_0(-t-s)[(1-P_0)iL_1-P_1iL_0]\sum_{m=0}^{\infty}(s^m/m!)f_m(\alpha_p)e^{i\mathbf{G}\cdot\mathbf{R}_I}\ . \tag{B14}$$

Since $U_0(-t-s)(-P_0iL_1-P_1iL_0)\sum_{m=0}^{\infty}s^mf_m(\alpha_p)\exp(i\mathbf{G}\cdot\mathbf{R}_I)/m!$ on the rhs of Eq. (B14) is independent of the phonon variable $Q(\mathbf{k},j)$ and the $\mathbf{F}_{\mathbf{P}_I}$, Eq. (27), is linear in $Q(\mathbf{k},j)$ this part does not contribute to $\boldsymbol{\phi}_{\mathbf{G}}(t)$. Thus we may replace $F_{\mathbf{G},1}(-t)$ by

$$F_{\mathbf{G},1}(-t)=-\int_0^{-t}dsU_0(-t-s)\left[\sum_{\mathbf{k},j}Q(\mathbf{k},j)\nabla_{\mathbf{R}_I}F(\mathbf{R}_I;\mathbf{k},j)\right]\cdot\nabla_{\mathbf{P}_I}g(s,\alpha_p)e^{i\mathbf{G}\cdot\mathbf{R}_I}\ , \tag{B15}$$

where we retained only a relevant term linear in $Q(\mathbf{k},j)$ and

$$g(s,\alpha_p)\equiv\sum_{m=0}^{\infty}(s^m/m!)f_m(\alpha_p)\ . \tag{B16}$$

Applying Eq. (B7) to Eq. (B15) and taking the interproduct with $\mathbf{F}_{\mathbf{P}_I}$, we obtain, after some algebraic manipulations,

$$\phi_{\mathbf{G}}(t)=i(k_BTn^2/NMM_I)\sum_{\mathbf{k},j,\mathbf{G}_0}2H(\mathbf{k},j\mid\mathbf{G}_0,\mathbf{G}_0-\mathbf{G})\mathbf{G}\cdot(\mathbf{G}-\mathbf{k}-\mathbf{G}_0)(\mathbf{k}+\mathbf{G}_0)$$
$$\times\int_0^{-t}ds\cos[\omega(\mathbf{k},j)(t+s)]\left\langle g'(s,-\alpha_p)e^{i(\mathbf{k}+\mathbf{G}_0)\cdot\mathbf{P}_I/M_I(t+s)}\right\rangle_0\ , \tag{B17}$$

where $g'(s,-\alpha_p)$ means the value of $\partial g(s,x)/\partial x$ at $x=-\alpha_p$ and for $\mathbf{H}(\mathbf{k},j\mid\mathbf{G}_0,\mathbf{G}_0')$ see Eq. (19).

From Eq. (B13) we see that the first few $f_m(\alpha_p)$'s are as follows:

$$\begin{aligned}&f_0(\alpha_p)=\alpha_p,\ f_1(\alpha_p)=\alpha_p^2-\langle\alpha_p^2\rangle\ ,\\&f_2(\alpha_p)=\alpha_p^3-\alpha_p\langle\alpha_p^2\rangle\ ,\\&f_3(\alpha_p)=\alpha_p^4-\alpha_p^2\langle\alpha_p^2\rangle-(\langle\alpha_p^4\rangle-\langle\alpha_p^2\rangle^2)\ .\end{aligned} \tag{B18}$$

From this, it is not difficult to show that

$$g(s,\alpha_p)=\alpha_pe^{\alpha_ps}-\int_0^s ds'e^{\alpha_ps'}\sum_{m=0}^{\infty}[C_{2m}/(2m)!](s-s')^{2m}$$
$$\equiv\alpha_pe^{\alpha_ps}-\int_0^s ds'e^{\alpha_ps'}H_G(s-s')\ , \tag{B19}$$

where

$$C_0=\langle\alpha_p^2\rangle=(-k_BTG^2/M_I)\tilde{C}_0(\tilde{C}_0=1)\equiv-r\ ,$$
$$C_2=\langle\alpha_p^4\rangle-\langle\alpha_p^2\rangle^2=(-r)^2\tilde{C}_2(\tilde{C}_2=3!!-1=2)\ ,$$

and in general

$$C_{2m}=\langle\alpha_p^{2(m+1)}\rangle-\sum_{n=1}^{m}\langle\alpha_p^{2n}\rangle C_{2m-2n}$$
$$=(-r)^{m+1}\left[(2m+1)!!-\sum_{n=1}^{m}(2n-1)!!\tilde{C}_{2m-2n}\right]\ , \tag{B20}$$

with $r=k_BTG^2/M_I$.[27] In deriving Eq. (B20) the Gaussian property of the variable α_p is used. With use of the relation (B20) we can derive an integral equation for $H_G(t)$, defined in Eq. (B19) as

$$H_G(t)=re^{-rt^2/2}(-1+rt^2)$$
$$+\int_0^t dsH_G(s)r(t-s)e^{-r(t-s)^2/2}\ , \tag{B21}$$

or, after partial integration

$$r^2t^2=\int_0^t ds\dot{H}_G(s)e^{-rs^2/2+rst}\ . \tag{B22}$$

From the integral equation we see that $H_G(t)=-r+r^2t^2-\cdots$ for short time and it goes to zero faster than $\exp(-rt^2/2)$. At present we have not solved the equation. However from a numerical point of view, $H_G(t)$ is easily obtained from Eq. (B20) in the form of Taylor expansion around $t=0$. From Eqs. (B19), (B17), and (36) we finally obtain

$$\phi_{\mathbf{G}}(t)=i(k_BTn^2/NMM_I)\sum_{\mathbf{k},j,\mathbf{G}_0}2H(\mathbf{k},j\mid\mathbf{G}_0,\mathbf{G}_0-\mathbf{G})\mathbf{G}_0\cdot(\mathbf{G}-\mathbf{k}-\mathbf{G}_0)(\mathbf{k}+\mathbf{G}_0)$$
$$\times\int_0^{-t}ds\cos[\omega(\mathbf{k},j)(t+s)]\left[\{1-(k_BTs/M_I)[sG^2-\mathbf{G}\cdot(\mathbf{k}+\mathbf{G}_0)(t+s)]\}\right.$$
$$\times e^{-(k_BT/2M_I)[(\mathbf{k}+\mathbf{G}_0)(t+s)-s\mathbf{G}]^2}$$
$$\left.-\int_0^s ds's'H_G(s-s')e^{-(k_BT/2M_I)[(\mathbf{k}+\mathbf{G}_0)(t+s)-s'\mathbf{G}]^2}\right]\ . \tag{B23}$$

It can be readily checked from Eq. (B23) that for the isotropic Debye model $\phi_{\mathbf{G}}(t)$ is independent of the transverse phonon modes.

[1]*Diffusion in Solids: Recent Development,* edited by A. S. Nowick and J. J. Burton (Academic, New York, 1975); *Diffusion in Crystalline Solids,* edited by G. E. Murch and A. S. Nowick (Academic, New York, 1984); *Mass Transport in Solids,* Vol. 97 of *NATO Advanced Studies Institute Series B,* edited by F. Beniere and C. R. A. Catlow (Plenum, New York, 1983).

[2]*Fast Ion Transport in Solids,* edited by P. Vashista, J. N. Mundy, and G. K. Shenoy (North-Holland, Amsterdam, 1979); *Hydrogen in Metals: Basic Properties,* Vol. 28 of *Topics in Applied Physics,* edited by G. Alefeld and J. Völk (Springer, Berlin, 1978).

[3]W. Dietrich, P. Fulde, and I. Peschel, Adv. Phys. **29**, 527 (1980).

[4]C. P. Flynn, *Point Defects and Diffusion* (Clarendon, Oxford, 1972), Chap. 6.

[5]G. H. Vineyard, J. Phys. Chem. Solids **3**, 121 (1957).

[6]C. P. Flynn, Phys. Rev. **171**, 682 (1968). See also, *Point Defects and Diffusion,* Ref. 4, Chap. 7.

[7]P. Fulde, L. Pietronero, W. R. Schneider, and S. Strassler, Phys. Rev. Lett. **35**, 1776 (1975).

[8]W. Dietrich, I. Peschel, and W. R. Schneider, Z. Phys. B **27**, 177 (1977); H. Risken and H. D. Vollmer, *ibid.* **31**, 209 (1978); T. Munakata and A. Tsurui, *ibid.* **34**, 203 (1979).

[9]T. Munakata, Prog. Theor. Phys. **73**, 570 (1985).

[10]H. Mori, Prog. Theor. Phys. **33**, 423 (1965).

[11]For lattice dynamics see A. A. Maradudin, E. W. Montroll, C. H. Weiss, and I. P. Ipatova, *Theory of Lattice Dynamics in the Harmonic Approximation* (Academic, New York, 1971).

[12]A set of dynamical variables **A** with infinite dimension has been used in dynamical theory of liquids. See A. Z. Akcasu and J. J. Duderstadt, Phys. Rev. **188**, 479 (1969) and J. J. Duderstadt and A. Z. Akcasu, Phys. Rev. A **1**, 905 (1970).

[13]K. Kawasaki, Ann. Phys. **61**, 1 (1970).

[14]P. A. Egelstaff, *An Introduction to Liquid State* (Academic, New York, 1967).

[15]P. B. Visscher, Phys. Rev. B **14**, 347 (1976); M. Buttiker, E. P. Harris, and R. Landauer, *ibid.* **28**, 1268 (1983).

[16]H. A. Kramers, Physica **54**, 284 (1940).

[17]W. G. Kleppmann and R. Zeyher, Phys. Rev. B **22**, 6044 (1980).

[18]B. Calmeri and A. Nitzan, J. Chem. Phys. **79**, 393 (1983).

[19]R. F. Grote and J. T. Hynes, J. Chem. Phys. **77**, 3736 (1982).

[20]T. Munakata, Prog. Theor. Phys. **73**, 826 (1985).

[21]T. Munakata and T. Kawakatsu, Prog. Theor. Phys. **74**, 262 (1985); T. Munakata, *ibid.* **75**, 747 (1986).

[22]M. Abramowitz and I. A. Stegun, *Handbook of Mathematical Functions* (Dover, New York, 1970).

[23]E. Ben-Jacob, D. J. Bergman, B. J. Matkowsky, and Z. Schuss, Phys. Rev. A **26**, 2805 (1982).

[24]For the Markovian Langevin equation the VAF is calculated by many authors (see Ref. 8).

[25]G. DeLorenzi, C. P. Flynn, and G. Jacucci, Phys. Rev. B **30**, 5430 (1984); G. H. Vineyard and J. A. Krumhansl, *ibid.* **31**, 4929 (1985).

[26]For soliton (kink) diffusion see J. A. Combs and S. Yip, Phys. Rev. B **29**, 438 (1984), and the references cited therein.

[27]$n!!=n(n-2)\times\cdots\times 4\times 2(n$: even) and $n!!=n(n-2)\times\cdots\times 3\times 1(n$: odd).