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Isotope Effect in Diffusion

H. R. GLYDE*
Division of Pure Physics, National Research Council of Canada, Ottawa 7, Canada

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A derivation of the classical jump rate Γ for tracer diffusion aimed at a clear expression for the mass dependence of the frequency factor $\tilde{\nu}$ is presented. The derivation is effected without using the usual collective normal coordinates which usually combine the masses in a complicated way. $\tilde{\nu}$ depends explicitly on the mass of the surrounding host atoms (as well as on the tracer-atom mass) if these atoms must move to new equilibrium positions after the jump. $\tilde{\nu}$ then has much the same form as suggested for a many-atom jump process. The contribution of the surrounding atoms is reduced (increased) for light (heavy) tracer atoms.

I. INTRODUCTION

RECENTLY, with the advent of accurate isotope-effect measurements,[1–3] there has been renewed interest in the mass dependence of the atomic jump rate Γ. These experiments often find that Γ is not always simply proportional to $m_1^{-1/2}$, where m_1 is the tracer atom mass, for a single-atom mechanism. Mundy *et al.*[2] have suggested an empirical connection between the departure from $\Gamma \propto m_1^{-1/2}$ and the activation volume ΔV.

The purpose of this paper is to present a derivation of Γ aimed at clear presentation of its mass dependence and the factors which determine it. This is done without using the usual normal coordinates and frequencies. Although these collective coordinates enable a compact development of Γ, the mass dependence is contained in a product of frequencies which is not easy to analyze. As the mass originates in the kinetic part of Γ, a more transparent expression is obtained by integrating this part directly rather than introducing mass-weighted or normal coordinates.

The best known of the many discussions[4–7] of Γ is that due to Vineyard,[7] followed by the discussion of the isotope effect by LeClaire.[8] For continuity, we follow as closely as possible the notation in these papers. A classical crystal in thermal equilibrium only is considered.

II. DERIVATION OF THE JUMP RATE Γ

A. Physical Description

We denote the total crystal potential by $\Phi(\mathbf{x})$. For some configurations $\mathbf{x}$, $\Phi(\mathbf{x})$ will have a minimum. We denote two such minimum (wells) by A and B. Physically, if we are considering self-diffusion by the vacancy mechanism, these wells correspond to all atoms localized about their respective lattice points with one site vacant (A); and again all atoms localized but now with the vacancy at an adjacent site (B).

In going from A to B, the system must pass through regions of increased $\Phi(\mathbf{x})$. Along one such path the increase in $\Phi(\mathbf{x})$ required will be least. We call the point $\mathbf{x}$ in configuration space along this minimum path where $\Phi(\mathbf{x})$ has its maximum the saddle point P. For migrations from A to B along this path, P marks a natural boundary between A and B. Through P we draw a surface S that is perpendicular to lines of constant $\Phi(\mathbf{x})$. This means that S will pass through points of maximum $\Phi(\mathbf{x})$ along all paths from A to B, and so forms a natural boundary between A and B. If the system is going from A to B we may say it is in B when S is crossed. (In the present treatment no discussion of the process beyond S is given.) Finally, we define a unit vector $\mathbf{p}$ that is parallel to $\mathbf{S}$ at P. As S is fixed by $\Phi(\mathbf{x})$, $\mathbf{p}$ can depend only on $\Phi(\mathbf{x})$.

In a classical crystal in thermal equilibrium, the probability of observing a fluctuation such that the system is at position $\mathbf{x}$ to $\mathbf{x}+d\mathbf{x}$ with velocity in the range $\dot{\mathbf{x}}$ to $\dot{\mathbf{x}}+d\dot{\mathbf{x}}$ is given by

$$\rho(\mathbf{x},\dot{\mathbf{x}})d\mathbf{x}d\dot{\mathbf{x}}=\rho_0 e^{-\beta\Phi(\mathbf{x})}\exp\Big[-\tfrac{1}{2}\beta\sum_{i\alpha}^{3N} m_i(\dot{x}_i^{\alpha})^2\Big]d\mathbf{x}d\dot{\mathbf{x}}, \tag{1}$$

where ρ_0 is a constant, $\beta=(kT)^{-1}$, k is Boltzmann's constant, and T is the absolute temperature. Thus, the rate of passage from A to B (which we suppose is limited by the barrier through which S passes) is given by the probability of observing a local coordinate fluctuation to a region $d\mathbf{S}$ of S with positive system velocity $\dot{\mathbf{x}}\cdot d\mathbf{S}\geq 0$ so that the system passes through S to B. The rate Γ is then

$$\Gamma=I/Q, \tag{2}$$

where

$$I=\rho_0\int_{\substack{\dot{\mathbf{x}}\\(\dot{\mathbf{x}}\cdot d\mathbf{S})\geq 0}}\int_S (\dot{\mathbf{x}}\cdot d\mathbf{S})\exp\Big[-\tfrac{1}{2}\beta\sum_{i\alpha}^{3N} m_i(\dot{x}_i^{\alpha})^2\Big]e^{-\beta\Phi(\mathbf{x}_S)}d\dot{\mathbf{x}} \tag{3}$$

is the current through S, and

$$Q=\rho_0\int_A\int_{\dot{\mathbf{x}}} e^{-\beta\Phi(\mathbf{x})}\exp\Big[-\tfrac{1}{2}\beta\sum_{i\alpha}^{3N} m_i(\dot{x}_i^{\alpha})^2\Big]d\dot{\mathbf{x}}d\mathbf{x} \tag{4}$$

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* Present address: School of Mathematical and Physical Sciences, University of Sussex, Brighton, England.

[1] N. L. Peterson and S. J. Rothman, Phys. Rev. **163**, 645 (1967); A. P. Batra, *ibid.* **159**, 487 (1967).

[2] L. N. Mundy, L. W. Barr, and F. A. Smith, Phil. Mag. **14**, 785 (1966), and references cited therein.

[3] N. L. Peterson, Phys. Rev. **136**, A568 (1964).

[4] J. H. Weiner, Phys. Rev. **169**, 570 (1968).

[5] W. M. Franklin, J. Phys. Chem. Solids **28**, 2216 (1967).

[6] H. R. Glyde, Rev. Mod. Phys. **39**, 373 (1967), and references cited there.

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

[8] A. D. LeClaire, Phil. Mag. **14**, 1271 (1966).

is essentially a normalizing constant giving the number of points originally in region A. At this point, all the "physics" of this essentially phenomenological treatment has been introduced. The situation discussed is identical to that considered by Vineyard and the remainder involves only integration.

B. Integrations

To integrate Q, we expand $\Phi(\mathbf{x})$ about $\mathbf{x}_A$, the minimum of well A, and extend the integration to ∞. (This extension should introduce little error as most of Q comes from near $\mathbf{x}_A$.) Keeping terms in $\Phi(\mathbf{x})$ up to second order only and using a standard matrix integration formula,[9] we obtain

$$Q=\rho_0\prod_i m_i^{-1/2}\left(\frac{2\pi}{\beta}\right)^{3N/2} e^{-\beta\Phi(\mathbf{x}_A)} \times\int_{\mathbf{x}}\exp(-\beta/2)(\mathbf{x}-\mathbf{x}_A)\cdot\mathbf{A}\cdot(\mathbf{x}-\mathbf{x}_A)d\mathbf{x}$$

$$=\rho_0 e^{-\beta\Phi(\mathbf{x}_A)}\prod_i m_i^{-1/2}\left(\frac{2\pi}{\beta}\right)^{6N/2}|\mathbf{A}|^{-1/2}, \qquad (5)$$

where $A_{ij}{}^{\alpha\beta}\equiv(\partial^2\Phi/\partial x_i{}^\alpha\partial x_j{}^\beta)_{\mathbf{x}_A}$, and $|\mathbf{A}|$ is the determinant of $\mathbf{A}$. The error introduced in keeping only second-order terms in $\Phi(\mathbf{x})$ is numerical only. It will be small if the anharmonic terms are small with respect to the harmonic over regions of $\mathbf{x}$ where Q is significant.

Similarly, to integrate I over S we expand $\Phi(\mathbf{x}_S)$ in the surface S about $\mathbf{x}_P$ so that

$$I=\rho_0 e^{-\beta\Phi(\mathbf{x}_P)}\int_S\int_{\dot{\mathbf{x}}}\exp[-\tfrac{1}{2}\beta(\mathbf{x}'-\mathbf{x}_P)\cdot\mathbf{A}^{+}\cdot(\mathbf{x}'-\mathbf{x}_P)] \times(\dot{\mathbf{x}}\cdot d\mathbf{S})\exp[-\tfrac{1}{2}\beta\dot{\mathbf{x}}\cdot\mathbf{m}\cdot\dot{\mathbf{x}}]d\dot{\mathbf{x}}, \qquad (6)$$

where the primed $(\mathbf{x}'-\mathbf{x}_P)$ denotes that the displacements are restricted to S, and $A^{+}{}_{ij}{}^{\alpha\beta}\equiv(\partial^2\Phi/\partial x_i{}^\alpha\partial x_j{}^\beta)_{x_P}$. Although, in general, all the x_i are involved in a displacement in S, S is a surface with $3N-1$ degrees of freedom. There is thus one condition of constraint $f(x'_1{}^\alpha\cdots x'_{3N}{}^\beta)=0$ among the $3N$ $x_i{}^\alpha$ when they are confined to S. This constraint is most easily accounted for by transforming to a new set of coordinates $\xi_1,\cdots,\xi_{3N}$ chosen so that one of them, ξ_1 say, is constant for motion in S. As we need only small displacements from P, these ξ_k can be related to the $(x-x_P)_i{}^\alpha$ by a linear transformation,

$$(x-x_P)_i{}^\alpha=\sum_k^{3N}c_{ik}{}^\alpha\xi_k=\sum_k^{3N}(\mathbf{i}^\alpha\cdot\mathbf{k})\xi_k, \qquad (7)$$

where $\mathbf{i}^\alpha$ and $\mathbf{k}$ are unit vectors of the original and new coordinate systems, respectively. Clearly, we must choose ξ_1 parallel to $\mathbf{p}$ so that it is constant for a displacement $d\mathbf{S}$ at P. For convenience we also choose the ξ_k system to be an orthogonal one, so that $\mathbf{c}$ is an orthogonal matrix ($\mathbf{c}^{-1}=\mathbf{c}^T$; $|\mathbf{c}|=1$), and set $\xi_1=\xi_p$.

If we write $d\mathbf{S}=\mathbf{p}|dS|$, then $(\dot{\mathbf{x}}\cdot d\mathbf{S})$ and the restriction $\dot{\mathbf{x}}\cdot d\mathbf{S}\geq 0$ is

$$(\dot{\mathbf{x}}\cdot d\mathbf{S})=(\dot{\mathbf{x}}\cdot\mathbf{p})|d\mathbf{S}|=\dot{\xi}_p|d\mathbf{S}|, \qquad (8)$$

with the restriction $\dot{\xi}_p\geq 0$ in the new coordinate system. We may then write (6) as

$$I=\rho_0 e^{-\beta\Phi(\mathbf{x}_P)}I_K I_S. \qquad (9)$$

Here I_K is the integration over the kinetic terms which, using (7) and (8) and the matrix integration in Appendix A, is

$$I_K=\int_{-\infty}^{\infty}\cdots\int_0^{\infty}\dot{\xi}_p\exp[-\tfrac{1}{2}\beta\dot{\boldsymbol{\xi}}\cdot\mathbf{C}\cdot\dot{\boldsymbol{\xi}}]d\dot{\boldsymbol{\xi}}$$

$$=\frac{1}{2\pi}\left(\frac{2\pi}{\beta}\right)^{(3N+1)/2}\prod_i m_i^{-1/2}[\sum_i m_i^{-1/2}(c_{ip}{}^\alpha)^2]^{1/2}, \qquad (10)$$

where $\mathbf{C}=\mathbf{c}\cdot\mathbf{m}\cdot\mathbf{c}$. I_S is the integration over S about P. Introducing the δ function $\delta(\xi_p)$ so that we may integrate over all coordinates, we obtain[10]

$$I_S=\int_{\mathbf{x}}|d\mathbf{S}|\exp[-\tfrac{1}{2}\beta(\mathbf{x}'-\mathbf{x}_P)\cdot\mathbf{A}^{+}\cdot(\mathbf{x}'-\mathbf{x}_P)]$$

$$=\int_{\xi}d\boldsymbol{\xi}\delta(\xi_p)\exp[-\tfrac{1}{2}\beta\boldsymbol{\xi}\cdot\mathbf{G}\cdot\boldsymbol{\xi}]$$

$$=(2\pi/\beta)^{(3N-1)/2}(G_{pp}{}^{\mathrm{cof}})^{-1/2}, \qquad (11)$$

where $G_{pp}{}^{\mathrm{cof}}$ is the cofactor of element G_{pp} in $\mathbf{G}=\mathbf{c}\cdot\mathbf{A}^{+}\cdot\mathbf{c}$, i.e., the determinant of $G_{kk'}=\sum_{ij\alpha\beta}c_{ki}{}^\alpha A_{ij}{}^{+}c_{jk'}{}^\beta$ with the pth row and column missing.

Collecting (9)–(11) to obtain I and using (5) for Q,

$$\Gamma=\frac{I}{Q}=\frac{1}{2\pi}[\sum_{i\alpha}^{3N}m_i^{-1}(c_{ip}{}^\alpha)^2]^{1/2}\left(\frac{|\mathbf{A}|}{(\mathbf{c}\cdot\mathbf{A}^{+}\cdot\mathbf{c})_{pp}{}^{\mathrm{cof}}}\right)^{1/2} \times\exp\{-\beta[\Phi(\mathbf{x}_P)-\Phi(\mathbf{x}_A)]\}$$

$$=\tilde{\nu}\exp\{-\beta[\Phi(\mathbf{x}_P)-\Phi(\mathbf{x}_A)]\}, \qquad (12)$$

where, since $|\mathbf{A}|$ and $(\mathbf{c}\cdot\mathbf{A}\cdot\mathbf{c})_{pp}{}^{\mathrm{cof}}$ are determinants of order $3N$ and $3N-1$ in the force constants, respectively, $\tilde{\nu}$ has the dimensions of a frequency.

III. DISCUSSION

A. Mass Dependence

As A_{ij} and $c_{ik}{}^\alpha$ do not contain the mass,

$$\tilde{\nu}(m)\propto[\sum_{i\alpha=1}^{3N}m_i^{-1}(c_{ip}{}^\alpha)^2]^{1/2}$$

$$=m_1^{-1/2}\left[d_{1p}{}^2+\sum_{i\neq 1}^{N}\left(\frac{m_1}{m_i}\right)d_{ip}{}^2\right]^{1/2}, \qquad (13)$$

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[9] A. C. Aitkin, in *Determinants and Matrices* (Wiley-Interscience, Inc., New York, 1954), p. 138.

[10] See Ref. 4, Eq. (2.17), for integration (and references cited there).

where m_1 is the tracer-atom mass and $d_{ip}^2 \equiv \sum_{\alpha=1}^3 \times (c_{ip}^\alpha)^2$ is the total displacement of solvent atom i along $\mathbf{p}$.

To discuss the physical implications of (13) we consider the vacancy mechanism. If there were no relaxation about either the vacancy or tracer atom, then before and after the vacancy-tracer exchange the surrounding atoms would take up the same positions. They would not need to migrate to new relaxed positions during the jump. Clearly, as they need not migrate anywhere, their velocity at P is unimportant and, on the average, their projection along $\mathbf{p}$ (or any vector) will be zero. As only the tracer atom must move in a specific direction, $d_{ip} = \delta_{1i}$ and $\tilde{\nu} \propto m_1^{-1/2}$. In this case the $\boldsymbol{\xi}$ coordinates can be the original $\mathbf{x}$ system (all $d_{ik} = \delta_{ik}$) so that

$$\Gamma = (1/2\pi m_1^{1/2})[|\mathbf{A}|/(\mathbf{A}^+)_{pp}{}^{\mathrm{cof}}]^{1/2} e^{-\beta[\Phi(\mathbf{x}_P)-\Phi(\mathbf{x}_A)]}. \quad (14)$$

Equation (14) has been quoted previously[11] and we see here that it is valid only in the limit that the surrounding atoms return exactly to their original positions after the jump.

If there is relaxation about either the vacancy or the tracer or both, this relaxation must change to a new form after the tracer-vacancy exchange. Some surrounding atoms must then be travelling in a specific direction during the jump (at P) as they move toward their new equilibrium positions. In this case, their projection along $\mathbf{p}$ will not be zero, and $d_{ip} \neq 0$. (Equivalently, we may say they must pass through S.) From (13), $\tilde{\nu}$ now depends on the mass of the surrounding atoms in much the same way as has been suggested for many-atom jump mechanisms. The number of atoms involved and the magnitude of d_{ip}^2 we should expect to be approximately proportional to the change in the relaxation, approximately proportional to ΔV_f for self-diffusion.

The effect of the relaxation on $\tilde{\nu}$ also depends on the ratio m_1/m_i. For light tracers, the effects of relaxation are reduced. In the limit $m_1/m_i \ll 1$ we always expect $\tilde{\nu} \propto m_1^{-1/2}$ (aside from quantum effects[8]). For heavy tracers, the effects are increased and in the limit $m_1/m_i \gg 1$ we expect no mass dependence as suggested in a model calculation by Rockmore and Turner.[12]

B. Expression for ΔK

Isotope experiments, which measure the ratio D^α/D^β for two isotopes α and β, are usually analyzed using

$$\begin{aligned} D^\alpha/D^\beta - 1 &= f(\Gamma^\alpha/\Gamma^\beta - 1) \\ &= f\Delta K[(m_\beta/m_\alpha)^{1/2} - 1], \end{aligned} \quad (15)$$

where f is the usual correlation factor and $\Delta K \equiv (\Gamma^\alpha/\Gamma^\beta - 1)/[(m_\beta/m_\alpha)^{1/2} - 1]$. Using (12), there appears to be no universally convenient expression for $\Gamma^\alpha/\Gamma^\beta$. Some forms, writing all $m_i = m_s$, the solvent atom mass, are

$$\frac{\Gamma^\alpha}{\Gamma^\beta} = \left(\frac{m_\beta}{m_\alpha}\right)^{1/2} \left[1 + \frac{m_\alpha}{m_s} \sum_{i\neq1}^{N} \left(\frac{d_{ip}}{d_{1p}}\right)^2\right]^{1/2} \Bigg/ \left[1 + \frac{m_\beta}{m_s} \sum_{i\neq1}^{N} \left(\frac{d_{ip}^2}{d_{1p}}\right)\right]^{1/2} \quad (16)$$

or, using $\sum_{i=1}^N d_{ip}^2 = 1$,

$$\frac{\Gamma^\alpha}{\Gamma^\beta} = \left[1 + \left(\frac{m_s}{m_\alpha} - 1\right) d_{1p}^2\right]^{1/2} \Bigg/ \left[1 + \left(\frac{m_s}{m_\beta} - 1\right) d_{1p}^2\right]^{1/2}. \quad (17)$$

Expression (17) clearly shows the dependence of the ratio $\Gamma^\alpha/\Gamma^\beta$ on d_{ip}^2 and the ratio m_α/m_s. It is also convenient for isotope effects in self-diffusion, as the second term in each square bracket is small so that both the numerator and denominator may be expanded. This gives

$$\Gamma^\alpha/\Gamma^\beta \approx 1 + \tfrac{1}{2} m_s (m_\alpha^{-1} - m_\beta^{-1}) d_{1p}^2 \quad (18)$$

and

$$\Delta K \approx \frac{\tfrac{1}{2} m_s (m_\alpha^{-1} - m_\beta^{-1}) d_{1p}^2}{(m_\beta/m_\alpha)^{1/2} - 1}. \quad (19)$$

For the case[2] of Na^{22} and Na^{24} in Na^{23}, direct substitution of the mass numbers in (19) gives

$$\Delta K \approx \frac{0.0435}{0.0440} d_{1p}^2 \approx d_{1p}^2 = 1 - \sum_{i\neq1}^{N} d_{ip}^2. \quad (20)$$

Mundy *et al.* find that $\Delta K = 0.505 \pm 0.02$ in Na. Using (20), this ΔK suggests that the sum of the distances that the surrounding atoms i must migrate to their new equilibrium positions, $\sum_{i\neq1} d_{ip}^2$, is approximately equal to the distance that the tracer atom moves as it goes to the adjacent site. In self-diffusion, the chief reason the surrounding atoms must migrate with the tracer is that the relaxation around the vacancy must move to a new site as the vacancy goes to a new site. The observed[13] activation volume is $\Delta V = \Delta V_f + \Delta V_m = 0.52$. Although we expect a proportional relation between ΔV_f and

$$1 - \sum_{i\neq1}^{N} d_{ip}^2,$$

there is no reason why they should be equal.

Equation (20),

$$\Delta K \approx 1 - \sum_{i\neq1}^{N} d_{ip}^2,$$

should hold well for most self-diffusion cases and Eq. (19) in impurity cases, provided $0.5 \leq m_s/m_\alpha \leq 1.5$.

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[11] Reference 6, Eq. (27).

[12] D. M. Rockmore and R. E. Turner, Physica **29**, 873 (1963).

[13] N. H. Nachtrieb, J. A. Weil, E. Catalano, and A. W. Lawson, J. Chem. Phys. **20**, 1185 (1952).

C. Comparison with Previous Treatments

The above differs from Vineyard's treatment in two respects. First, Vineyard uses the coordinates $y_i=x_i/\sqrt{m_i}$ and appears to define the velocity in I as $\dot{y}$ rather than $\dot{x}$. Secondly, normal coordinates are used to do the coordinate integrations and $\tilde{\nu}$ is expressed in terms of frequencies. This has the advantage of getting the mass terms out of the kinetic integrations, where they originate, but introduces them into the configuration integrations in a way which is not easily analyzable and in a way which changes when the tracer mass is changed. [The d_{ik} here are defined solely in terms of $\Phi(\mathbf{x})$ and are unaffected by mass changes.] The present $\tilde{\nu}$ can be expressed in terms of frequencies ω_i, which are independent of mass, defined by

$$\prod_i^{3N}\omega_i=|\mathbf{A}|^{1/2}\quad\text{and}\quad\prod_i^{3N-1}\omega_i^{+}=[(\mathbf{c}\cdot\mathbf{A}^{+}\cdot\mathbf{c})_{pp}{}^{\mathrm{cof}}]^{1/2}.$$

LeClaire[8] has already clearly recognized the connection between relaxation and ΔK. It was necessary there, however, to assume that the kinetic energy of each atom in the "decomposition mode" was proportional to the distance it must migrate to its new equilibrium position. Ordinarily, as the equilibrium correlation function $\langle x\dot{x}\rangle=0$, no correlation between kinetic energy and position in any real mode is expected. The connection between ΔK and relaxation is obtained more directly here but is no different from that stated by LeClarie.[14]

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APPENDIX

To integrate

$$I_K=\int_{-\infty}^{\infty}\cdots\int_0^{\infty}\dot{\xi}_p\exp[-\tfrac{1}{2}\beta\dot{\boldsymbol{\xi}}\cdot\mathbf{C}\cdot\dot{\boldsymbol{\xi}}]d\dot{\xi}_p\cdots d\dot{\xi}_{3N}\tag{21}$$

(where $\dot{\xi}_p\equiv\dot{\xi}_1$) we break up the matrix C into parts involving $\dot{\xi}_p$ only:

$$\dot{\boldsymbol{\xi}}\cdot\mathbf{C}\cdot\dot{\boldsymbol{\xi}}=(\dot{\xi}_p\dot{\xi}_y)\begin{pmatrix}C_{pp} & \mathbf{C}_{py}\\ \mathbf{C}_{yp} & \mathbf{C}_{yy}\end{pmatrix}\begin{pmatrix}\dot{\xi}_p\\ \dot{\xi}_y\end{pmatrix},\tag{22}$$

where $\dot{\xi}_y$ includes all components $\dot{\xi}_k\neq\dot{\xi}_p$.

Integrating over all components except $\dot{\xi}_p$, we have[15]

$$I_K=\left(\frac{2\pi}{\beta}\right)^{(3N-1)/2}|\mathbf{C}_{yy}|^{1/2}\int_0^{\infty}\dot{\xi}_p \times\exp[-\tfrac{1}{2}\beta\dot{\xi}_p(C_{pp}-\mathbf{C}_{py}\cdot\mathbf{C}_{yy}{}^{-1}\cdot\mathbf{C}_{yp})\dot{\xi}_p]d\dot{\xi}_p.\tag{23}$$

We now define a matrix $\boldsymbol{\Gamma}$ inverse to $\mathbf{C}$ such that $\mathbf{C}\cdot\boldsymbol{\Gamma}=\boldsymbol{\Gamma}\cdot\mathbf{C}=\mathbf{1}$; i.e.,

$$\begin{pmatrix}C_{pp} & \mathbf{C}_{py}\\ \mathbf{C}_{yp} & \mathbf{C}_{yy}\end{pmatrix}\begin{pmatrix}\Gamma_{pp} & \boldsymbol{\Gamma}_{py}\\ \boldsymbol{\Gamma}_{yp} & \boldsymbol{\Gamma}_{yy}\end{pmatrix}=\begin{pmatrix}1 & 0\\ 0 & 1\end{pmatrix}.\tag{24}$$

Using this definition directly, we have[15]

$$\Gamma_{pp}{}^{-1}=C_{pp}-\mathbf{C}_{py}\cdot\mathbf{C}_{yy}{}^{-1}\mathbf{C}_{yp},\tag{25}$$

where $\Gamma_{pp}{}^{-1}$ is defined by $\Gamma_{pp}\Gamma_{pp}{}^{-1}=1$.

Since Γ_{pp} is a single element (i.e., just a number) $(\Gamma_{pp}{}^{-1})^{-1}=\Gamma_{pp}$. Also, by definition of an inverse,

$$\Gamma_{pp}=|\mathbf{C}_{yy}|/|\mathbf{C}|\tag{26}$$

and

$$\boldsymbol{\Gamma}=\mathbf{C}^{-1}=(\mathbf{c}\cdot\mathbf{m}\cdot\mathbf{c})^{-1}=\mathbf{c}\cdot\mathbf{m}^{-1}\cdot\mathbf{c},$$

so that

$$\Gamma_{pp}=(\mathbf{c}\cdot\mathbf{m}^{-1}\cdot\mathbf{c})_{pp}=\sum_{i\alpha}^{3N}(c_{ip}{}^{\alpha})^2m_i{}^{-1}.\tag{27}$$

Thus, using (25)–(27), I_K becomes

$$\begin{aligned}I_K&=\left(\frac{2\pi}{\beta}\right)^{(3N-1)/2}|\mathbf{C}_{yy}|^{-1/2}\int_0^{\infty}\dot{\xi}_p\times\exp[-\tfrac{1}{2}\beta\dot{\xi}_p\Gamma_{pp}{}^{-1}\dot{\xi}_p]d\dot{\xi}_p\\ &=\left(\frac{2\pi}{\beta}\right)^{(3N-1)/2}|\mathbf{C}_{yy}|^{-1/2}(\beta\Gamma_{pp}{}^{-1})^{-1}\\ &=\frac{1}{2\pi}\left(\frac{2\pi}{\beta}\right)^{(3N+1)/2}|\mathbf{C}_{yy}|^{-1/2}\Gamma_{pp}{}^{1/2}\Gamma_{pp}{}^{1/2}\\ &=\frac{1}{2\pi}\left(\frac{2\pi}{\beta}\right)^{(3N+1)/2}|\mathbf{C}|^{-1/2}[\sum_{i\alpha}^{3N}(c_{ip}{}^{\alpha})^2m_i{}^{-1}]^{1/2},\end{aligned}$$

and $|\mathbf{C}|^{-1/2}=\prod_i m_i{}^{-1/2}$ since $\mathbf{c}$ is unitary.

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[14] Recently, C. P. Flynn [Phys. Rev. **171**, 691 (1968)], using a "dynamical" approach, has obtained an isotope effect displaying the same dependence on the ratio of the tracer to solvent atom mass as noted here in Sec. III A. However, his result is expressed in terms of fractional kinetic energies and is not directly related to the displacements required of the surrounding atoms. Also, its validity relies upon the harmonic approximation, whereas the present result is independent of any potential approximation.

[15] T. R. Koehler, Phys. Rev. **141**, 281 (1966), Eqs. (6)–(9).