Statistical Mechanics of Thermotransport of a Heavy Impurity in an Insulating Solid *

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A kinetic equation is derived for the singlet distribution function for a heavy impurity in a lattice of lighter atoms in a temperature gradient. In the one dimensional case the equation can be solved to find formal expressions for the jump probability and hence the heat of transport, q^*, for a single vacancy jump of the impurity. q^* is the sum of the enthalpy of activation, a term involving only averaging in an equilibrium ensemble, and two non-equilibrium terms involving time correlation functions. The most important non-equilibrium term concerns the correlation between the force on the impurity and a microscopic heat flux. A plausible extension to three dimensions is suggested and the relation to earlier isothermal and non-isothermal theories is indicated.

1. Introduction

If a one component solid of atoms, A, and vacancies, V, is subject to a temperature gradient then the equations of irreversible thermodynamics give for the flux of atoms, $\boldsymbol{J}_{\mathrm{A}}$, relative to the local crystalline lattice[1,2]

$$\boldsymbol{J}_{\mathrm{A}} = L_{\mathrm{AA}}[kT(\nabla c_{\mathrm{V}}/c_{\mathrm{V}} - \nabla c_{\mathrm{A}}/c_{\mathrm{A}}) + Q_{\mathrm{A}}^{*}\nabla T/T], \quad (1.1)$$

provided the vacancies are few enough that activity coefficients are unity. c_{A} and c_{V} are concentrations (site fractions), L_{AA} is a phenomenological coefficient, and Q_{A}^{*} is the thermodynamic heat of transport. The reduced heat flux, $\boldsymbol{J}_q$, in an isothermal system is given by

$$\boldsymbol{J}_q = Q_{\mathrm{A}}^{*}\,\boldsymbol{J}_{\mathrm{A}}, \quad \nabla T = 0. \quad (1.2)$$

We consider only diffusion on lattices of cubic symmetry in this paper.

It is plausible that the probability per unit time that an atom will jump from a plane at mean temperature T to one at mean temperature $T + \Delta T$, say $w(T, T + \Delta T)$, can be written in the form

$$w(T, T + \Delta T) = w_0(T)[1 + \Delta w(T)\,\Delta T] \quad (1.3)$$

where $w_0(T)$ is the isothermal jump probability at temperature T and the equation defines Δw. If we calculate the flux of atoms between the adjacent planes at T and $T + \Delta T$ and assume that the vacancies are so dilute that we need consider only isolated independent vacancies, i.e. neglect vacancy pairs etc., then[2] by retaining only terms of first order in gradients, an equation of the form of Eq. (1.1) is found in which Q_{A}^{*} is replaced by the "heat of transport for a single jump", q^*, defined by

$$q^* = \Delta h_{\mathrm{m}} - 2\,k\,T^2\,\Delta w, \quad (1.4)$$

$$\Delta h_{\mathrm{m}} = k\,T^2\left(\frac{\partial \log w_0(T)}{\partial T}\right)_p. \quad (1.5)$$

Δh_{m} is the enthalpy of activation for migration.

We consider the calculation of Δw for jumps in insulating solids close to the melting point where classical statistical mechanics is valid. Much of the meagre experimental data[2] is for the thermoelectric power or Soret effect in crystals with Schottky or Frenkel defects. These relatively simple systems are our ultimate objective. The relevant multicomponent equations replacing (1.1) and (1.2) for these systems are well-known[1,2] and need not be repeated here. There are then several different quantities like q^* because the jump probabilities are different for different species, and are also modified by the presence of nearby defects. The calculation of the thermodynamic heats, $\boldsymbol{Q}^*$, in terms of the heats of transport for individual jumps, q^*, is relatively simple for dilute systems but there is little agreement on how to calculate q^*. By contrast the calculation of isothermal jump rates, w_0, and the relation between the different methods of calculation is much better understood. In order to make plain the reasons for adopting the formalism which follows we complete this introduction by briefly re-

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viewing the calculations of w_0 and also certain theories of the heat of transport. Only vacancy jumps are considered in this paper.

The theories of w_0 fall into two broad groups. In the first and most highly developed group equilibrium statistics are employed. The formalisms of RICE[3] and VINEYARD[4], recently shown[5] to be identical up to a certain late point in the calculation, are prime examples. LIDIARD[6] concluded that the extension of the Vineyard calculation to calculate Q^* through the isothermal Eq. (1.2) leads to $q^* \leqq \Delta h_m$ if one stays strictly within the limitations imposed by the formalism. The main limitation is that there is no description of the evolution of the correlations between atomic motions which lead to the saddle point configuration, and therefore no description of the flow of energy up to and after the attainment of this configuration[6]. Such a description is presumably essential to an isothermal calculation of Q^*, but how it is to be introduced into these theories is not known. However, SCHOTTKY[7] has initiated the extension of the Rice calculation to the nonisothermal calculation of Q^* by allowing for a distribution of phonon energies within a relaxation time approximation. HUNTINGTON[8] gave a more intuitive description of the meaning of this calculation. The effect arises from the scattering of the phonon flux by the vacancy which intensifies the thermal gradient in its neighbourhood. However, he concludes that this effect will be practically negligible in a three dimensional lattice.

The difficulties noted by Lidiard perhaps arise in part from the difficulty of trying to add an element of non-equilibrium statistical mechanics to a formalism firmly based on equilibrium theory. It is therefore interesting to reconsider the second group of theories of w_0 which are based on non-equilibrium statistical mechanics. They are exemplified by the calculations of PRIGOGINE and BAK[9], ROCKMORE and TURNER[10], and KRAMERS[11, 12]. They avoid equilibrium methods by use of, for example, a SMOLUCHOWSKI[10] or FOKKER-PLANCK[11, 12] equation for the temporal evolution of the distribution function for the coordinates of the jumping atom. These equations contain a friction constant whose evaluation is very difficult. It requires the calculation of a time dependent correlation function involving the correlation of the motion of the jumping atom with the motions of the other atoms in a small time interval. It is essentially this kind of dynamical correlation effect which has proved so difficult, and possibly relatively more important, to include in the non-isothermal case. We therefore consider in this paper the extension of the non-equilibrium theories to calculate Δw.

The other theories of thermal diffusion[2] are not so clearly related to the isothermal formalisms as that of Schottky. Two are particularly relevant. In the theory of FIKS[13] the activated atom exchanges momentum with the phonon flux. Although the method of calculation is formally incorrect because it equates crystal momentum with real momentum[8] this does not necessarily mean the effect is negligible. Part of the difficulty is to incorporate it in the jump rate theory in a logical manner and obtain a formal expression for evaluation.

The other relevant theory is the very well-known calculation of WIRTZ[14]. It is assumed that the energy of activation is taken up in three parts at the mean temperatures of the initial site, the final site, and the point midway between. The three energies are not unambiguously defined. The original form leads to the conclusion $q^* \leqq \Delta h_m$, which is not in agreement with results for several ionic crystals[15–18]. By contrast the Schottky theory permits $q^* > \Delta h_m$.

Since no attempt is made to describe time dependent molecular correlations the Wirtz theory is related to the equilibrium group of isothermal theories but with the idea of local equilibrium in a tem-

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perature gradient added. Wirtz applied similar ideas to liquids[19, 20]. In the Kirkwood transport theory for liquids as applied to thermal diffusion[21] the distribution function is the sum of a time-independent local equilibrium part and a non-equilibrium perturbation. The former leads to a contribution to Q^* involving only equilibrium ensemble averages and the latter to a truly non-equilibrium part involving in principle the calculation of time-dependent molecular correlations. This division into two terms is now known to be rigorous[22]. Kirkwood implies that the equilibrium term corresponds to the Wirtz liquid theory which he interprets as neglecting all non-equilibrium aspects. One might expect a similar division into equilibrium and non-equilibrium terms in q^* for the solid, but this has not so far been done.

The ideas of local equilibrium, phonon scattering, and description of molecular correlations over a period of time all find places in the formalism which follows. Presumably they are essential ingredients of any theory. Additional effects occur in metals because the migrating nucleus can interact with conduction electrons[8]. We attempt to show that for a heavy impurity Δw contains two principle contributions. One is a purely equilibrium part related to Wirtz theory as interpreted above. The other contains a time-dependent correlation function descriptive of the scattering of the local heat flux by the impurity during its passage to the transition state, and is related to Fiks idea.

In Section 2 the derivation of kinetic equations for the heavy atom is outlined. The modified Fokker-Planck equation is solved in Section 3 to find a formal expression for the jump rate in one dimension. In Section 4 the relation between equilibrium and non-equilibrium isothermal calculations is indicated and the result for q^* reviewed in this light. A plausible speculation on the form of the formal result for q^* in three dimensions is then made.

2. The Kinetic Equation for the Jumping Atom

The formal derivation of isothermal kinetic equations for the jumping atom of the kinds used earlier[10, 11] can be made by the Zwanzig projection operator method[23] which was not then available. The advantages of this method are that the extension to the nonisothermal case is easy and the approximations are well defined. It is clear from the derivations that these kinetic equations are valid with any degree of certainty only when the mass of the atom of interest is greater than that of those with which it interacts. They are then, in the isothermal case, equations of Brownian motion theory[12, 24]. We therefore call the heavy impurity atoms Brownian atoms (or B-atoms), and the remaining atoms light atoms.

The analogous nonisothermal equation for fluids was first given by ZUBAREV and BASHKIROV[25]. A more satisfactory derivation using the projection operator method by MAZO[26] led to some additional terms. Since all the most difficult points are discussed there[26] the outline of our derivation of the equation for solids, made independently of MAZO's recent work, can be quite brief. In addition to the absence of hydrodynamic terms the final result differs slightly from the fluid one because of the lattice periodicity.

We consider a system of $N+1$ atoms (or ions) comprising the B-atom of interest which is labelled 0, and N other atoms, not necessarily all of the same kind, labelled 1, 2, ..., N. $\boldsymbol{R}_i$, $\boldsymbol{p}_i$ denote the position and momentum coordinates of atom number i, and $\{\boldsymbol{N}\}$ denotes the set of position and momentum coordinates of the atoms labelled $i=1, 2, \ldots, N$. Similarly we use the abbreviation

$$\mathrm{d}\{\boldsymbol{N}\} = \prod_{i=1}^{N} \mathrm{d}\boldsymbol{R}_i \, \mathrm{d}\boldsymbol{p}_i \,. \tag{2.1}$$

Polyatomic molecules or ions are not considered.

The Liouville operator, L, for the system is given, in the absence of extrenal fields, by

$$i\,L = \sum_{i=0}^{N} \left\{ \frac{\boldsymbol{p}_i}{m_i} \cdot \nabla_i + \boldsymbol{F}_i \cdot \frac{\partial}{\partial p_i} \right\}. \tag{2.2}$$

$\boldsymbol{F}_i$ is the force on atom i whose mass is m_i. The gradient operators in configuration and momentum space are denoted by ∇ and $\partial/\partial\boldsymbol{p}$ respectively. The distribution function, f, for the probability of a

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particular set of positions and momenta for the $N+1$ atoms satisfies the Liouville equation,

$$\frac{i\,\partial f(t)}{\partial t} = L f(t)\,, \tag{2.3}$$

and is normalized to unity.

We define a projection operator P, to be specified more fully below, which acts on some subset of coordinates and has the property

$$P^2 G = P G \tag{2.4}$$

where G is an arbitrary phase function. Furthermore, we define ϱ_1 and ϱ_2 by

$$\varrho_1(t) = P f(t)\,, \tag{2.5}$$

$$\varrho_2(t) = (1-P) f(t)\,. \tag{2.6}$$

By application of the operators P and $(1-P)$ to the Liouville equation it can be shown[23] that $\varrho_1(t)$ satisfies the equation

$$\begin{aligned}\frac{i\,\partial \varrho_1(t)}{\partial t} = {} & P L \varrho_1(t) + P L \exp[-(1-P)\,i L t]\,\varrho_2(0) \\ & - P i L \int_0^t \mathrm{d}s \exp[-(1-P)\,i L s] \\ & \times (1-P) L \varrho_1(t-s)\,.\end{aligned} \tag{2.7}$$

This identity can be used to derive kinetic equations for the two specific distribution functions defined by

$$f_1(\boldsymbol{R}_0, \boldsymbol{p}_0, t) = \int \mathrm{d}\{\boldsymbol{N}\} f(t)\,, \tag{2.8}$$

$$n_1(\boldsymbol{R}_0, t) = \int \mathrm{d}\boldsymbol{p}_0\, f_1(\boldsymbol{R}_0, \boldsymbol{p}_0, t) \tag{2.9}$$

which specify the probability of finding the B atom of interest at $\boldsymbol{R}_0$, $\boldsymbol{p}_0$, or at $\boldsymbol{R}_0$ independent of its momentum, respectively.

The relevant projection operator is defined by

$$P = (f^{(0)}/f_1^{(0)}) \int \mathrm{d}\{\boldsymbol{N}\}\,. \tag{2.10}$$

The local equilibrium distribution function, $f^{(0)}$, appearing here is defined by

$$\begin{aligned} f^{(0)} = A \exp\{ & -\sum_{i=0}^{N} \beta(\boldsymbol{R}_i)\,[p_i^2/2\,m_i - \mu_i(\boldsymbol{R}_i) \\ & + \sum_{\substack{k=0\\k \neq i}}^{N} \tfrac{1}{2} V(R_{ik})]\}\,. \end{aligned} \tag{2.11}$$

A is a normalization factor, μ_i is the chemical potential of atom i, β is $(k\,T)^{-1}$, $V(R_{ik})$ is the pair potential for the atoms i and k a distance R_{ik} apart, and R_{ik} is defined by

$$\boldsymbol{R}_{ik} = \boldsymbol{R}_i - \boldsymbol{R}_k\,. \tag{2.12}$$

$f_1^{(0)}$ is calculated from $f^{(0)}$ by Eq. (2.8). With these definitions Eq. (2.5) yields

$$\varrho_1(t) = (f^{(0)}/f_1^{(0)})\, f_1(t)\,. \tag{2.13}$$

The system may be imagined to be maintained in a steady state prior to $t=0$ by the application of appropriate external forces and heat resevoirs[27]. These are removed at $t=0$ and the approach to equilibrium studied. We therefore choose[26–27] $f(0)$ to be $f^{(0)}$. For this initial condition one obtains

$$\varrho_1(0) = f(0)\,, \quad \varrho_2(0) = 0\,. \tag{2.14}$$

The third term in Eq. (2.7) is therefore zero. To evaluate the remaining terms we next define L_0 and L_{N} by

$$i L_0 = \frac{\boldsymbol{p}_0}{m_0} \cdot \nabla_0 + \boldsymbol{F}_0 \cdot \frac{\partial}{\partial \boldsymbol{p}_0}\,, \tag{2.15}$$

$$i L_{\mathrm{N}} = i L - i L_0\,, \tag{2.16}$$

and define λ by $\lambda^2 = m/m_0$ were m is the largest of the masses of the light atoms. Then L_0 is on average $0(\lambda)$ times smaller than L_{N}[26]. An essential step in the derivation is then to expand the exponential operator in the last term of Eq. (2.7) in powers of L_0 and retain only zero order terms[26, 28]. Straightforward evaluation of the retained terms gives the result:

$$\begin{aligned} & \left(\frac{\partial}{\partial t} + \frac{\boldsymbol{p}_0}{m_0} \cdot \nabla_0 + \langle \boldsymbol{F}_0 \rangle_0 \cdot \frac{\partial}{\partial \boldsymbol{p}_0}\right) f_1(\boldsymbol{R}_0, \boldsymbol{p}_0, t) \\ & \quad = \frac{\partial}{\partial \boldsymbol{p}_0} \cdot \left\{\left[\boldsymbol{\zeta}' \cdot \left(k\,T \frac{\partial}{\partial \boldsymbol{p}_0} + \frac{\boldsymbol{p}_0}{m_0}\right)\right.\right. \\ & \qquad \left.\left. + \boldsymbol{\eta} \cdot \nabla \log T\right] f_1(\boldsymbol{R}_0, \boldsymbol{p}_0, t)\right\} \end{aligned} \tag{2.17}$$

where the friction constants are defined by

$$\boldsymbol{\zeta}' = \boldsymbol{\zeta} + \boldsymbol{\eta}' \cdot \nabla \log T \tag{2.18}$$

$$\boldsymbol{\zeta} = \beta \int_0^\infty \mathrm{d}s \langle \boldsymbol{F}_0\, \boldsymbol{F}_0(-s) \rangle_0\,, \tag{2.19}$$

$$\boldsymbol{\eta}' = \beta^2 \int_0^\infty \mathrm{d}s \langle \boldsymbol{F}_0\, \boldsymbol{B}(-s) \rangle_0\,, \tag{2.20}$$

$$\begin{aligned} \boldsymbol{\eta} & = \beta \int_0^\infty \mathrm{d}s \;\; \langle \boldsymbol{F}_0\, \boldsymbol{J}_{\mathrm{H}}(-s) \rangle_0 - \beta \langle \boldsymbol{F}_0\, \boldsymbol{A} \rangle_0 \\ & = \boldsymbol{\eta}^{(1)} + \boldsymbol{\eta}^{(0)}\,, \end{aligned} \tag{2.21}$$

and the remaining definitions are

$$\boldsymbol{F}_0 = \boldsymbol{F}_0 - \langle \boldsymbol{F}_0 \rangle_0\,, \tag{2.22}$$

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$$\boldsymbol{A} = \boldsymbol{A} - \langle \boldsymbol{A} \rangle_0 , \tag{2.23}$$

$$\boldsymbol{B} = \boldsymbol{A}\boldsymbol{F}_0 - \langle \boldsymbol{A}\boldsymbol{F}_0 \rangle_0 , \tag{2.24}$$

$$\boldsymbol{A} = \sum_{i=0}^{N} \mathbf{R}_i (p_i^2/2\, m_i - \bar{H}_i + \sum_{k=0}^{N} \tfrac{1}{2} V(R_{ik})) , \tag{2.25}$$

$$\boldsymbol{J}_{\mathrm{H}} = \sum_{i=1}^{N} [(p_i^2/2\, m_i - \bar{H}_i)\, \boldsymbol{l} \tag{2.26}$$

$$+ \tfrac{1}{2} \sum_{k=0}^{N} (V(R_{ik})\, \boldsymbol{l} - \mathbf{R}_{ki} \nabla_k V(R_{ki}))] , (\tilde{\boldsymbol{p}}_i/m_i)$$

$$\boldsymbol{X}(s) = \exp(i L_{\mathrm{N}} s)\, \boldsymbol{X} , \quad \boldsymbol{X} \equiv \boldsymbol{X}(0) , \tag{2.27}$$

$$\langle \boldsymbol{X} \rangle_0 = \int \mathrm{d}\{\boldsymbol{N}\} f^{(\mathrm{e})}(\{\boldsymbol{N}\}, \mathbf{R}_0 , \boldsymbol{p}_0)/f_1^{(\mathrm{e})}(\mathbf{R}_0 , \boldsymbol{p}_0)\, \boldsymbol{X} . \tag{2.28}$$

(b) There is one other corraction to Eq. (2.26). It shold read like this:

$$\boldsymbol{J}_{\mathrm{H}} = \sum_{i=0}^{N} [(p_i^2/2\, m_i - \bar{H}_i)\, \boldsymbol{l} + \tfrac{1}{2} \sum_{k=0}^{N} (V(R_{ik})\, \boldsymbol{l}$$

$$- \mathbf{R}_{ki} \nabla_k V(R_{ki}))] \cdot \boldsymbol{p}_i/u_i . \tag{2.26}$$

$\boldsymbol{X}$ denotes any phase function. The superscript (e) signifies an equilibrium distribution function. In the computation of the averages in Eqs. (2.19)—(2.21) the B particle number 0 is held fixed during the time evolution, as implied by Eq. (2.27). $\boldsymbol{J}_{\mathrm{H}}$ is the microscopic heat flux, and $\bar{H}_i$ is the partial molecular heat content of the species of molecule i.

Three additional approximations were made in writing the final result. (1) Only terms linear in ∇T were retained. The vectors $\boldsymbol{R}_i$ in $\boldsymbol{A}$, Eq. (2.25), are from the origin which is at mean temperature, T, and this is taken to be the lattice site from which the B-atom will escape in Section 3. (2) Certain terms[26] in $\nabla_T \mu$ were neglected as can be justified in detail for the application which follows. (3) It was assumed that the time correlation functions decay very rapidly compared with the variation of f_1 in order to convert the non-Markoffian equation derived to the Markoffian one above[26]. Finally we note that the friction constants ζ, η are independent of the momentum of the B atom but not necessarily of its position.

For $\nabla T = 0$ Eq. (2.17) is the familiar Fokker-Planck equation. The corresponding Smoluchowski equation for n_1 is derived from it[12] by the coordinate transformations $\boldsymbol{P} = \boldsymbol{R}_0 + \boldsymbol{p}_0 \zeta^{-1}$, $\boldsymbol{\rho} = \boldsymbol{p}_0/m_0$ followed by integration with respect to ϱ from $-\infty$ to ∞. The result is

$$\frac{\partial n_1}{\partial t} = \nabla_0 \cdot (k\, T\, m_0 \nabla_0 n_1 + \langle \boldsymbol{F}_0 \rangle_0 n_1$$

$$+ \eta \nabla \log T\, n_1) \zeta^{-1} \tag{2.29}$$

for $t \gg m/\zeta$ and $\varDelta \gg (k\, T\, m/\zeta^2)^{1/2}$ where $\varDelta$ is of the order of the distance of significant variations in $\langle \boldsymbol{F}_0 \rangle_0$. This derivation is really only satisfactory if ζ is independent of position. To avoid this assumption one can derive a similar equation for n_1 directly by the projection operator method. Since in the rest of the paper we concentrate on the Fokker-Planck equation and only refer to the Smoluchowski equation occasionally we shall not give details.

In the problem at hand all the averages over position coordinates are to be taken as restricted to all configurations of each atom about a particular lattice site. In particular there is a vacancy next to the B atom. This does not significantly complicate the derivation which, up to this point, is fairly unambiguous for a heavy atom. The difficulties begin when appropriate solutions of the kinetic equation and explicit formula for the friction constants are sought.

In the remainder of the paper we can drop the subscripts zero on $\boldsymbol{F}_0$, $\boldsymbol{p}_0$, m_0.

3. Calculation of Jump Rate

Eq. (2.17) with $\nabla T = 0$ was solved by KRAMERS[11, 12] for an atom escaping from a potential well in one dimension. The calculation shows exceptionally clearly the relation between equilibrium and non-equilibrium theories. The object of this section is to generalize the calculation to the non-isothermal case.

We begin the calculation in three dimensions. For a solid of cubic symmetry the temperature gradient can be conveniently taken as a one dimensional one along the x axis. Suppose the B-atom is vibrating about a lattice A site (the origin) and is to jump to a vacant nearest neighbour site B. The sites lie on the x axis at $x_{\mathrm{A}} = 0$ and $x_{\mathrm{B}} > 0$. Fig. 1 sketches the potential of the mean force experienced by the B-atom in passing along the x axis. The saddle point is at x_{C}.

If the B-atom could not leave the well at A then in the limit of long times a stationary distribution satisfying Eq. (2.17) would be valid for B anywhere in the well. If the B-atom can escape to site B and the barrier is large compared with $k\,T$ then the stationary distribution still obtains to a high degree

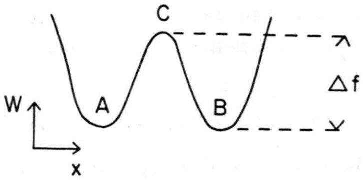

Fig. 1. Potential, W, of the mean force on the B-atom passing from site A to site B along the x axis in absence of a temperature gradient.

of accuracy near A but there will be deviations near C. The solution can be written in the form

$$f_1(\boldsymbol{R}, \boldsymbol{p}, t) = f_1^{(s)}(\boldsymbol{R}, \boldsymbol{p})\, G(\boldsymbol{R}, \boldsymbol{p}) . \tag{3.1}$$

$f_1^{(s)}$ is the stationary distribution valid near A and the correction function G must satisfy the boundary conditions

$$\begin{aligned} G(\boldsymbol{R}, \boldsymbol{p}) &\simeq 1 , \quad \boldsymbol{R} \sim \boldsymbol{R}_{\mathrm{A}} , \\ G(\boldsymbol{R}, \boldsymbol{p}) &\simeq 0 , \quad x \gg x_{\mathrm{C}} . \end{aligned} \tag{3.2}$$

Eq. (3.1) contains the approximation that f_1 is stationary since G has been taken as independent of t. This is a good approximation for big enough potential barriers ($\Delta f \gtrsim 2 - 3\, k\, T$) where the rate of escape is small[9, 10].

Direct substitution shows that a stationary distribution, $f_1^{(s)}$, is given by

$$f_1^{(s)}(\boldsymbol{F}, \boldsymbol{p}) = \varphi(p)\, n_1^{(s)}(\boldsymbol{R}) , \tag{3.3}$$

$$\varphi(p) = C_{\mathrm{m}} \exp\{- p^2/2\, m\, k\, T\} , \tag{3.4}$$

$$n_1^{(s)}(\boldsymbol{R}) = C_{\mathrm{c}} \exp\left\{ - [W_1(R) + \frac{\mathrm{d} \log T}{\mathrm{d}x} \int_0^x \eta\, \mathrm{d}x]/k\, T \right\}$$

where W_1 is the singlet potential of mean force such that

$$- \nabla_{\mathrm{R}} W_1(\boldsymbol{R}) = \langle \boldsymbol{F}_0(\boldsymbol{R}) \rangle_0 , \tag{3.5}$$

and C_{m} and C_{c} are normalization constants. (One should show that the stationary solution is unique; compare the closely related barometric distribution problem where this has been done[29].) The kinetic equation is valid only to terms of first order in ∇T, and $f_1^{(s)}$ should be linearized when it is used.

The equation for G found by substituting (3.1) into (2.17) is difficult to solve in three dimensions but useful information comes from the following one dimensional solution. It is necessary to assume that none of the friction constants depend on position to solve the equation. It will also be assumed that $\langle F_0 \rangle_0$ can be approximated near x_{C} by

$$\langle F_0 \rangle_0 = (x - x_{\mathrm{C}})\, m\, \omega_{\mathrm{C}}^2 \tag{3.6}$$

where ω_{C} is a constant. The coordinate transformation

$$y = \frac{p}{m} - a(x - x_{\mathrm{C}}) + \eta \frac{\mathrm{d} \log T}{\mathrm{d}x} (m a - \zeta')^{-1} , \tag{3.7}$$

where a is defined as the positive[12] root of

$$a = m\, \omega_{\mathrm{C}}^2 / (m a - \zeta') , \tag{3.8}$$

then leads to the following differential equation

$$\frac{\mathrm{d}^2 G}{\mathrm{d}y^2} + A\, y \frac{\mathrm{d}G}{\mathrm{d}y} = 0 \tag{3.9}$$

where

$$A = (m a - \zeta')/m q , \tag{3.10}$$

$$q = k\, T\, \zeta'/m^2 . \tag{3.11}$$

The solution is found at once to be

$$G(y) = C_1 \int_{-\infty}^{y} \exp\{- A\, y'^2/2\}\, \mathrm{d}y' , \tag{3.12}$$

where

$$C_1^{-1} = \int_{-\infty}^{\infty} \exp\{- A\, y'^2/2\}\, \mathrm{d}y' = (2\, \pi/A)^{1/2} . \tag{3.13}$$

This satisfies the boundary conditions

$$\begin{aligned} G(y) &= 1 , \quad y = + \infty , \\ G(y) &= 0 , \quad y = - \infty . \end{aligned} \tag{3.14}$$

These are equivalent to Eq. (3.2) for a deep well which is already implied by the stationary assumption.

The expression for the jump probability is

$$w = j(x_{\mathrm{C}}) / \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} f_1(x, p)\, \mathrm{d}x\, \mathrm{d}p \tag{3.15}$$

where the flux is given by

$$\begin{aligned} j(x_{\mathrm{C}}) &= \int_{-\infty}^{\infty} \frac{p}{m} f_1(x_{\mathrm{C}}, p)\, \mathrm{d}p \\ &= C_{\mathrm{m}}\, C_{\mathrm{c}}\, k\, T\, n^{(s)}(x_{\mathrm{C}}) \int_{-\infty}^{\infty} \varphi(p) \left(\frac{\partial G}{\partial p} \right)_{x = x_{\mathrm{C}}} \mathrm{d}p . \end{aligned} \tag{3.16}$$

The last line follows by integration by parts. From Eq. (3.12) one finds

$$\exp\{- p^2/2\, m\, k\, T\} \left(\frac{\partial G}{\partial p} \right)_{x = x_{\mathrm{C}}} = m^{-1} C_1 \exp\{- a\, p^2/2\, q\, m^2\} \left\{ 1 + p\, \eta \frac{\mathrm{d}T}{\mathrm{d}x} D + 0\left(\left(\eta \frac{\mathrm{d}T}{\mathrm{d}x} \right)^2 \right) \right\} , \tag{3.17}$$

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[29] M. C. Wang, and G. E. Uhlenbeck, Rev. Mod. Phys. **17**, 323 [1945].

where D is independent of p, η, and $\mathrm{d}T/\mathrm{d}x$. Eqs. (3.16) and (3.17) yield the result

$$j(x_\mathrm{C}) = n^{(\mathrm{s})}(x_\mathrm{C})\,(k\,T\,C_\mathrm{c}\,C_\mathrm{m}\,C_1)\,(2\,\pi\,q/a)^{1/2}\,. \qquad (3.18)$$

The term in η does not contribute to j.

The main contribution to the integrand in the denominator of w, Eq. (3.15), is from near $x=0$ where $f_1^{(e)}$ is an adequate approximate to f_1. In the harmonic approximation we have

$$W_1(x) = \tfrac{1}{2}\,x^2\,m\,\omega_\mathrm{A}^2 + W_1(0) \qquad (3.19)$$

where the frequency ω_A can be determined from the force constants[5]. Evaluating the denominator with these approximations and using Eq. (3.18) the expression for w is:

$$w = \left(\frac{n^{(\mathrm{s})}(x_\mathrm{C})}{n^{(\mathrm{s})}(0)}\right)\left(\frac{\omega_\mathrm{A}}{2\,\pi}\right)\left(\frac{m\,a-\zeta'}{m\,a}\right)^{1/2}. \qquad (3.20)$$

a, ζ', and $n^{(\mathrm{s})}(x_\mathrm{C})$ all contain terms in ∇T. After linearization the final result is

$$w_0(T) = \left(\frac{\omega_\mathrm{A}}{2\,\pi}\right)\left(\frac{m\,a_0-\zeta}{m\,a_0}\right)^{1/2}\exp\{-\Delta f/k\,T\}\,, \qquad (3.21)$$

$$\Delta f = W_1(x_\mathrm{C}) - W_1(0)\,,$$

$$q^* - \Delta h_\mathrm{m} = x_\mathrm{C}^{-1}\int_0^{x_\mathrm{C}} \eta\,\mathrm{d}x + 2\,k\,T\,\eta'(x_\mathrm{C}[\zeta^2 + 4\,m\,\omega_\mathrm{C}^2]^{1/2})^{-1}\,. \qquad (3.22)$$

a_0 is the value of a when $\nabla T = 0$. Notice that the second term on the right comes from G which was evaluated assuming that ζ and η' were independent of position, whereas no such assumption was made for the first term which comes from $n_1^{(s)}$.

4. Discussion

In the limit of vanishing dynamical friction, $\zeta \to 0$, we obtain the equilibrium theory result as formulated by Wert[30,31]:

$$w_0(T) = (\omega_\mathrm{A}/2\,\pi)\exp\{-\Delta f/k\,T\}\,. \qquad (4.1)$$

This can be transformed to the expression of Glyde[5] referred to in Section 1 if required. The equilibrium analysis is equivalent to assuming $G=1$ and integrating between 0 and ∞ instead of $-\infty$ and ∞ to avoid the difficulty that there is no net flux in an equilibrium calculation. In the limit $\zeta \gg 2\,m\,\omega_\mathrm{C}$ we obtain an expression with a different (smaller) pre-exponential than the equilibrium theory:

$$w_0(T) = (m\,\omega_\mathrm{A}\,\omega_\mathrm{C}/2\,\pi\,\zeta)\exp\{-\Delta f/k\,T\}\,. \qquad (4.2)$$

This can be obtained directly from the Smoluchowski equation[11,12]. Rockmore and Turner[10] also solved the Smoluchowski equation but without assuming that f_1 is stationary or assuming $\Delta f \gg k\,T$. The result for $\Delta f \gg k\,T$ has a different pre-exponential from the Kramers result, Eq. (4.2), because the potential of mean force was assumed to be given by, Eq. (3.19) at all positions. Kramers' emphasis on obtaining an accurate solution near x_C seems more reasonable. The disadvantage of his analysis is that it is difficult to solve the non-stationary equation for G without assuming $\Delta f \gg k\,T$. If it is assumed that η is independent of x then the Rockmore Turner method can be used for the nonisothermal case. The term in q^* containing η is the same as that found above, but that containing η' is of course different.

We consider next the nonisothermal case in the light of the above. The term in η comes from $n^{(\mathrm{s})}(x_\mathrm{C})$, whereas the term in η' comes from G. η' is expected to be of minor importance because it describes more complicated higher order correlations than those in η, and it is actually zero for a homogeneous isotropic medium[26]. The terms in η contained in G did not contribute to the final result. It seems reasonable to expect that the properties of G will not be greatly different in three dimensions. Taking all these points into consideration suggests that a good first approximation for three dimensions will be to take $f_1 = f^{(\mathrm{s})}$ (i.e. $G=1$) and proceed as in the equilibrium theory[31] described above. The result is

$$q^* - \Delta h_\mathrm{m} = \iint \{x_\mathrm{C}^{-1}\int_0^{x_\mathrm{C}} \eta(x,y,z)\,\mathrm{d}x\} \times \exp\{-W_1(x_\mathrm{C},y,z)/k\,T\}\,\mathrm{d}y\,\mathrm{d}z\Big/\iint \times \exp\{-W_1(x_\mathrm{C},y,z)/k\,T\}\,\mathrm{d}y\,\mathrm{d}z\,. \qquad (4.3)$$

The expression for $w_0(T)$ is the same as Wert[30,31] or can be transformed to that of Glyde[5] for computation.

If the term in η' is *not* unimportant then the formal theory becomes much more difficult in three dimensions because different expressions will be obtained according to whether one works in the limit

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[30] C. Wert, Phys. Rev. **79**, 601 [1950].

[31] A. B. Lidiard, Handbuch der Physik **20**, 246 [1957]; our Eq. (3.23) is equivalent to Eq. (15.7) of Lidiard's exposition reduced to one dimension.

of large or small dynamical damping. A general solution for G in three dimensions valid in both limits and without assuming the friction constants are independent of postion has not been obtained even in the isothermal case. Unfortunately there does not seem to be clearcut guidance from theory or experiment as to which limit is the correct one. The problem is related to the theory of the isotope effect in diffusion[10]. An expression for ζ is required. Rockmore and Turner used an expression for ζ which neglects changes in force constants due to the impurity and completely neglects the presence of the vacancy. It is difficult to discover whether these approximations are excessive or whether ζ would still be independent of position if they were removed.

The equilibrium term, $\eta^{(0)}$, can be transformed to a form closely related to the equilibrium term in fluid theory[21, 22]. It is the analogue of the Wirtz theory[14] as interpreted in Section 1. The non-equilibrium term, $\eta^{(1)}$, clearly relates to the scattering of the local heat flux by the impurity on its path to the saddle point. By making similar assumptions to those of FIKS[13] the contribution to q^* is proportional to $\sigma T \varkappa / v$ as found by Fiks, where σ is the scattering cross-section, $\varkappa$ the thermal conductivity and v the velocity of sound. It is hoped that our expression can be used as a starting point for calculations which dispense with the dubious special assumptions noted in Section 1. The phonon scattering effect of SCHOTTKY[7] must also enter here. For a heavy isotope in a one dimensional lattice with linear nearest neighbour forces and no adjacent vacancy the method of calculation used[32] for ζ gives $\eta^{(1)} = 0$. However the calculations of the correlation function for thermal conductivity for such a system are well-known to lead to results not relevant at high temperatures where anharmonicity is vital for the existence of a finite conductivity. Other difficulties can arise because the characteristics of the time correlation function are slightly different from those familiar in the theory of diffusion and thermal conductivity. In the Taylor expansion in powers of time it is the coefficients of even powers which average to zero instead of odd ones. This also occurs in the theory of the heat of transport of dense fluids[22].

The method is limited to heavy impurities. The non-equilibrium jump rate theory of PRIGOGINE and BAK[9] does not have this limitation; in fact it appears to fail for heavy atoms[10]. The irreversibility enters through a non-linear interaction between the jumping atom, whose unperturbed motion is harmonic, and the rest of the lattice. This theory can also be extended to the non-isothermal case as will be discussed elsewhere. In the absence of a general formal expression for q^* comparable to the equilibrium expression for w_0 we believe it is useful to obtain expressions for those cases where well defined kinetic equations exist in order to provide starting points for calculation.

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[32] J. L. LEBOWITZ, and E. RUBIN, Phys. Rev. **131**, 2381 [1963].