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# Time correlation formula for the heat of transport associated with atom–vacancy exchange in a crystal

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## Abstract

Statistical mechanical expressions are derived for atom–vacancy exchange frequencies in a crystalline insulator with a gradient of temperature and for the heat flux associated with such exchanges in an isothermal system. The associated Onsager reciprocal relation is verified. A time correlation function expression is thus identified for the heat of transport,  $q^*$ , associated with a single atom–vacancy exchange. Here  $q^*$  is defined as in standard kinetic theories of non-isothermal matter transport in crystals. The expression for  $q^*$  is compared with an earlier one derived by Gillan through a calculation of the heat flux associated with an atom–vacancy exchange in an isothermal system. There are differences but numerical results from molecular dynamics simulations will be close when the fraction of unsuccessful jump attempts is small.

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## 1. Introduction

The formalism of non-equilibrium thermodynamics provides the standard phenomenological framework for the interpretation of experiments on matter transport in crystals with temperature gradients [1, 2]. Within this formalism a key parameter for each chemical species is its heat of transport. By virtue of the Onsager reciprocal relations the heat of transport not only characterizes part of the flux of the species that is proportional to the temperature gradient but is also the coefficient of proportionality between the heat flux and the atomic flux of the species in an isothermal system. This remarkable property means that there are two possible routes to a molecular-level calculation of the heat of transport.

Little progress towards a molecular theory of thermal diffusion in solids was made until Gillan [3] provided a formal expression, suitable for evaluation through molecular dynamics simulations, for the heat of transport associated with an atom–vacancy exchange in an insulator. A zero-temperature illustration of such a calculation was soon made [4] and it was also

shown [3, 5] how the expression could be made the basis of analytical calculations. Perhaps because the demands on computing time are heavy, it is only recently that the expression has been used for detailed finite-temperature simulations. Jones *et al* [6] have made molecular dynamics simulations for vacancy migration in solid argon at 30–60 K and determined the heats of transport associated with argon and solute atom jumps. Further simulations based on the Gillan formula are in progress for these and other systems (Grout and Lidiard, private communication 2000, Jacobs and Rycerz, private communication 2000). In the systems of interest the activation energies are large compared with  $kT$  and consequently defect jumps would rarely be observed on the timescale of a standard molecular dynamics simulation. The essential feature of Gillan's formulation is that it allows the use of a constrained molecular dynamics technique [7, 8], which is far more efficient.

The derivation of the Gillan formula follows the isothermal route and is based on the calculation of the heat flow associated with an atom–vacancy exchange in an isothermal system. It is not exact [3] but the derivation is highly plausible for systems where successive vacancy jumps are so far separated in time as to be dynamically independent, as will be the case when activation energy barriers are large compared with  $kT$ . In view of the recent interest in the heat of transport it seems timely to look at an analysis which makes closer contact with more recent formulations of the statistical mechanics of activated processes and also examines both calculation routes.

Most theoretical calculations of jump rates in isothermal solids have been made within the framework of the absolute rate theory (transition state theory) as formulated by Vineyard [9]. The rate theory uses equilibrium statistical mechanics to calculate the rate at which an appropriate reaction coordinate,  $\xi$ , reaches a critical value with a velocity,  $\dot{\xi}$ , of the correct sign to take the jumping atom towards its new site. The rate formula so derived is sometimes multiplied by a factor (the transmission coefficient) to correct for so-called unsuccessful jumps in which the reaction velocity subsequently changes sign and the atom returns to the vicinity of its original site without completing the attempted jump. The calculation of the transmission coefficient and the pursuit of formulations of rate processes which are firmly based in non-equilibrium statistical mechanics remained largely in abeyance until the advent of molecular dynamics simulations. An influential starting point has been work of Chandler [10], which generalized and expanded the time correlation function (TCF) approach to chemical reaction rate constants [11]; there are several reviews of activated processes from this point of view [12–14]. This newer framework has subsequently begun to appear in calculations of defect migration rates in isothermal systems [8, 15]. Here we shall extend this TCF approach to the heat of transport by obtaining formal expressions for the jump frequency for atom–vacancy exchange in a non-isothermal system and for the heat flux associated with an isothermal exchange. Our result for the heat of transport, like Gillan's [3], is based on classical statistical mechanics and is limited to an insulator in which the concentration of vacancies is very small so that only single independent vacancies need be considered. Extension to the simple interstitial mechanism would be straightforward.

We begin by describing in section 2 a simple phenomenological model defined in terms of site occupancies, atom–vacancy exchange frequencies and the kinetic equation which connects them. We also summarize how the effect of a temperature gradient on a jump frequency is usually parametrized. In the following section we establish a statistical mechanical analogue for the kinetic equation. Expressions for jump frequencies in systems both without and with a gradient of temperature are determined in section 4 by comparing the phenomenological and statistical mechanical expressions. The expression for the heat of transport is then discussed and compared with the result of Gillan [3].

## 2. The phenomenological model

Attention will be focused on two nearest-neighbour sites,  $A$  and  $B$ , one vacant and one occupied by an atom. The atom occasionally makes an activated jump from one site to the other. We assume, as is usually done in such discussions, that barriers have been introduced to prevent other atoms jumping into the vacant site. Let us suppose that site  $A$  is on lattice plane  $x$  and site  $B$  is on the plane  $x + a$ . The loss–gain equation for the occupancy of site  $A$  is

$$\frac{dp_A(t)}{dt} = -w_{\alpha+}p_A(t) + w_{\beta-}p_B(t) \quad (2.1)$$

in which  $p_A(t)$  is the probability that the atom is localized at site  $A$  at time  $t$  and  $w$  denotes a jump frequency of the atom. The jump frequency subscripts  $\alpha$  and  $\beta$  allow for the possibility that even in an equilibrium system jumps of the atom from  $A$  to  $B$  and from  $B$  to  $A$  may have different frequencies and therefore be of different ‘types’,  $\alpha$  and  $\beta$ , because of an asymmetry in the surroundings of the two sites. (An example of this distinction occurs for a dilute alloy when a host atom makes a jump which changes the separation of the vacancy from some nearby solute atom whose presence influences the jump frequency.) The subscript labels  $+$  and  $-$  signify that the jump takes the atom in the positive or negative direction along the  $x$ -axis, respectively. Since the sum of the probabilities  $p_A$  and  $p_B$  is unity, equation (2.1) can be solved; the result is

$$p_A(t) = \left( p_A(0) - \frac{w_{\beta-}}{\lambda_{\pm}} \right) e^{-\lambda_{\pm}t} + \frac{w_{\beta-}}{\lambda_{\pm}} \quad (2.2)$$

where

$$\lambda_{\pm} = w_{\alpha+} + w_{\beta-}. \quad (2.3)$$

Jump frequencies are always functions of local thermodynamic variables but if the system is not at thermodynamic equilibrium they can also depend on the gradients of these variables. Following Howard and Manning [16], we then write a jump frequency  $w_{\gamma\pm}$  as the value,  $w_{\gamma}$ , for a type  $\gamma$  jump in a uniform system which is in the thermodynamic state for the plane  $x + a/2$  midway between  $A$  and  $B$ , plus terms linear in gradients. When there is just a one-dimensional temperature gradient along the  $x$ -axis but no other thermodynamic forces (such as gradients of concentrations, stress or applied electrical potential) the expression is

$$w_{\gamma\pm} = w_{\gamma}(1 \pm aq_{\gamma}^*\nabla_x\beta/2) \quad (2.4)$$

where  $\beta$  is  $(kT)^{-1}$  and  $\nabla_x \equiv \partial/\partial x$ . The parameter  $q_{\gamma}^*$  defined by equation (2.4) is called the reduced heat of transport of a type  $\gamma$  jump. This name is used because, when the flux of atoms is calculated by kinetic arguments, assuming for simplicity just one kind of atom, and is compared with the expression for the flux assumed in non-equilibrium thermodynamics, it is found that  $q^*$  plays the role of the reduced heat of transport defined in the thermodynamic theory. In the general case the heats of transport of the thermodynamic theory are functions of the heats of transport for individual jumps defined in equation (2.4) and these functions have to be determined by kinetic theories [16, 17].

The later comparison of the phenomenological model, as summarized by equations (2.2)–(2.4), with the results of an approximate statistical mechanical treatment can be made only on a timescale which is appropriate for both descriptions. Both the phenomenological and the statistical descriptions do not hold for times less than some characteristic time  $\tau_r$ ; for times shorter than  $\tau_r$  a transient non-exponential decay will hold. On the other hand the statistical expression will be valid only for times short compared with both the characteristic time  $\tau_e$  for an appreciable change in the occupancy of site  $A$  towards its equilibrium value and also with

the much longer characteristic time for relaxation of the temperature gradient in a macroscopic system. Therefore, similarly to [14], we introduce a timescale  $\tau$ , such that

$$\lambda_{\pm}^{-1} = \tau_e \gg \tau \gg \tau_r \quad (2.5)$$

and take the time derivative of equation (2.2) on this timescale:

$$\frac{dp_A(t)}{dt} = -\lambda_{\pm} \left( p_A(0) - \frac{w_{\beta-}}{\lambda_{\pm}} \right) e^{-\lambda_{\pm} t} \xrightarrow{t \sim \tau} -\lambda_{\pm} p_A(0) + w_{\beta-}. \quad (2.6)$$

The later approximate statistical description will, however, be valid only to terms linear in deviations from thermodynamic equilibrium. Therefore, the expression, equation (2.4), for jump frequencies in a temperature gradient is substituted into equation (2.6) and terms of second order in deviations from thermodynamic equilibrium (i.e. terms proportional to  $\Delta p_A(0) \nabla_x \beta$ ) are neglected. The expression to be compared with the statistical treatment is then found to be

$$\frac{dp_A(\tau)}{d\tau} = -\lambda \Delta p_A(0) - \frac{a}{2} w_{\alpha} p_A (q_{\alpha}^* + q_{\beta}^*) \nabla_x \beta \quad (2.7)$$

where

$$\lambda = w_{\alpha} + w_{\beta} \quad (2.8)$$

$$\Delta p_A(0) = p_A(0) - p_A \quad (2.9)$$

and  $p_A (= w_{\beta}/\lambda)$  denotes the equilibrium probability.

### 3. Statistical mechanical treatment of the model

#### 3.1. Reaction coordinate and site occupancy

We employ a reaction coordinate,  $\xi$ , that is a function of the position of the hopping atom and some of its neighbours. The value  $\xi = 0$  defines the saddle plane and we suppose that  $\xi < 0$  when the atom is in the potential well centred on site  $A$ . A more complete definition of  $\xi$  is not unique [7]; an example is used in appendix A.4 in the course of estimating orders of magnitude but it is not needed elsewhere. We define two step functions,  $\theta_A$  and  $\theta_B$ , which divide the configuration space according to whether the atom is associated with site  $A$  ( $\xi < 0$ ) or with site  $B$  ( $\xi > 0$ ):

$$\begin{aligned} \theta_A(\xi) &= 1 & \xi < 0 \\ &= 0 & \xi > 0 \end{aligned} \quad (3.1)$$

$$\theta_A(\xi) + \theta_B(\xi) = 1. \quad (3.2)$$

The average value at time  $t$  of any dynamical variable  $X(\Gamma)$  which does not depend explicitly on time will be written as

$$\overline{X(t)} = \int d\Gamma X(\Gamma) f(\Gamma, t) = \int d\Gamma f(\Gamma, 0) X(\Gamma, t) \quad (3.3)$$

where  $\Gamma$  denotes the complete set of position and momentum coordinates of all the atoms. The distribution function  $f(\Gamma, t)$  satisfies the Liouville equation

$$\frac{\partial f(\Gamma, t)}{\partial t} = -iL f(\Gamma, t) \quad (3.4)$$

where  $L$  denotes the Liouville operator. The formal expression for  $X$  at time  $t$  in terms of its initial value  $X(\Gamma)$  is

$$X(\Gamma, t) = \exp(iLt) X(\Gamma). \quad (3.5)$$

The probability,  $p_i(t)$ , that the hopping atom is associated with site  $i$  is then given by

$$p_i(t) = \overline{\theta_i(t)} \quad i = A, B. \quad (3.6)$$

### 3.2. Local equilibrium

Our method of deriving a kinetic equation for the site occupancy  $\overline{\theta_A(t)}$  employs the idea of a local equilibrium distribution, often used in establishing expressions for thermal transport coefficients of fluids in the linear-response regime [18, 19]. The basic assumption is that for small deviations from thermodynamic equilibrium the instantaneous state always differs only slightly from a state of local equilibrium which can be described by a distribution function constructed very similarly to that for a system at equilibrium. Although the state of the system is very close to that described by the local equilibrium distribution function, this distribution is not a solution of the Liouville equation and cannot be used to predict transport properties. However, if we start off the ensemble with this distribution function at some instant we can expect that it will evolve in a very short time into a function that predicts the correct fluxes of heat and matter. That this procedure, due to Mori [20], gives correct results for calculating *linear* response transport coefficients of fluids is confirmed by all other theories, see for example [21]; we assume that the same is true here.

We first outline the construction of a local equilibrium distribution function for a closed constant-volume system, containing the two special sites  $A$  and  $B$ . We may suppose that the information about the state of the system at some time  $t$  is provided in the form of the current values of the ensemble averages of the internal energy density, the linear momentum density and the number densities of the various species of atom at every point  $\mathbf{r}$  in the system. We denote by  $A_m(\Gamma, \mathbf{r})$  the molecular expression for a typical local density  $A_m$ ; the set of densities is

$$A_m = \{H, \{g_\alpha\}, \{n_a\}, n_{hA}, n_{hB}\} \quad (3.7)$$

where  $H(\Gamma, \mathbf{r})$  is the energy density at  $\mathbf{r}$ ,  $\{g_\alpha(\Gamma, \mathbf{r})\}$  denotes the set of Cartesian components ( $\alpha = x, y, z$ ) of the linear momentum density  $\mathbf{g}(\Gamma, \mathbf{r})$ ,  $\{n_a(\Gamma, \mathbf{r})\}$  denotes the set of number densities of the various atomic species ( $a = 1, 2, 3 \dots$ ) and  $n_{hA}(\Gamma, \mathbf{r})$  and  $n_{hB}(\Gamma, \mathbf{r})$  are the number densities for the hopping atom  $h$  when it is associated with the site  $A$  and with the site  $B$  respectively. Here and elsewhere, the label  $a$  does not include species  $hA$  and  $hB$ . The use of  $\alpha$  to label both types of jump and Cartesian components will readily be distinguished by the context.

Explicit formulae for the various densities are as follows. The energy density is

$$H(\Gamma, \mathbf{r}) = \sum_i \delta(\mathbf{r} - \mathbf{r}_i) e_i(\Gamma) \quad (3.8)$$

where  $\mathbf{r}_i$  and  $e_i$  are the position and energy of atom  $i$ , respectively, and the summation is over every atom in the system. For a pairwise intermolecular potential the expression for  $e_i$  is

$$e_i = \mathbf{p}_i^2/2m_i + \frac{1}{2} \sum_{j \neq i} u(r_{ij}) \quad (3.9)$$

where  $\mathbf{p}_i$  is the momentum and  $m_i$  the mass of the atom, and  $u$  is a pair potential energy. The expressions for the other densities are

$$\mathbf{g}(\Gamma, \mathbf{r}) = \sum_i \mathbf{p}_i \delta(\mathbf{r} - \mathbf{r}_i) \quad (3.10)$$

$$n_a(\Gamma, \mathbf{r}) = \sum_{i \in a} \delta(\mathbf{r} - \mathbf{r}_i) \quad (3.11)$$

$$n_{hi}(\Gamma, \mathbf{r}) = \delta(\mathbf{r} - \mathbf{r}_h) \theta_i(\Gamma) \quad i = A, B. \quad (3.12)$$

In the last equation  $\mathbf{r}_h$  is the position of the hopping atom.

The local equilibrium distribution function,  $f_0(\Gamma, t)$ , for the state at time  $t$  is constructed by maximizing the entropy,

$$S(t) = -k \int d\Gamma f_0(\Gamma, t) \ln f_0(\Gamma, t) \quad (3.13)$$

subject to the constraints that  $f_0$  is normalized to unity and that the averages of the densities calculated from  $f_0$  must equal the exact values, i.e.

$$\langle A_m(\mathbf{r}) \rangle_{0t} = \overline{A_m(\mathbf{r}, t)} \quad (3.14)$$

where  $\langle \dots \rangle_{0t}$  denotes an average over  $f_0(\Gamma, t)$ . The result is

$$f_0(\Gamma, t) = Q_0(t)^{-1} \exp \left[ - \sum_m \int d\mathbf{r} \gamma_m(\mathbf{r}, t) A_m(\Gamma, \mathbf{r}) \right] \quad (3.15)$$

in which the  $\gamma_m(\mathbf{r}, t)$  and  $\ln Q_0(t)$  are Lagrange multipliers.

The expression for entropy found by substituting for  $\ln f_0$  from (3.15) into (3.13) can be used to determine an expression for the change in entropy due to infinitesimal changes in the mean local densities; from this the multipliers can be identified [22] as functional derivatives of the entropy,  $k\gamma_m(\mathbf{r}, t) = \delta S(t) / \delta \langle A_m(\mathbf{r}) \rangle_{0t}$ . These identities can be viewed as generalizations to a non-equilibrium system of standard thermodynamic relations when the following identifications are made:

$$\gamma_m = \{\beta, \{-\beta v_\alpha\}, \{-\zeta_a\}, -\zeta_{hA}, -\zeta_{hB}\} \quad (3.16)$$

where

$$\zeta_b = \beta(\mu_b - m_b v^2/2) \quad b = a, hA, hB. \quad (3.17)$$

Here  $\mathbf{v}(\mathbf{r}, t)$  is the local centre of mass velocity (equal to  $\langle \mathbf{g}(\mathbf{r}) \rangle_{0t} / M$  where  $M$  is the total mass of the system),  $\mu_b(\mathbf{r}, t)$  is the local chemical potential of species  $b$ ,  $m_b$  is the mass of a  $b$  atom and  $\beta(\mathbf{r}, t)$  is  $[kT(\mathbf{r}, t)]^{-1}$  where  $T(\mathbf{r}, t)$  is the local thermodynamic temperature. These identifications of the multipliers with local thermodynamic functions are standard, although the detailed arguments leading to them vary slightly, see for example section 20.1 of [22] and chapter 9 of [19].

For future use we note here the expression for an average over the local equilibrium distribution function for some dynamical variable  $X(\Gamma)$  when there are only very small deviations from thermodynamic equilibrium and the limit  $\mathbf{v} = 0$  is taken. In the expression for  $f_0(\Gamma, t)$  we first expand the thermodynamic functions  $\gamma_m(\mathbf{r})$  about their values  $\gamma_m \equiv \gamma_m(\mathbf{r}_0)$  for a uniform system in the thermodynamic state corresponding to the midpoint  $\mathbf{r}_0$  between sites  $A$  and  $B$ , and take the linear approximation

$$\gamma_m(\mathbf{r}, t) = \gamma_m(t) + (\mathbf{r} - \mathbf{r}_0) \cdot \nabla \gamma_m(t). \quad (3.18)$$

The final result, correct to first order in deviations from equilibrium, can then be written as

$$\Delta X(t) \equiv \langle X \rangle_{0t} - \langle X \rangle = \langle \delta X \delta \theta_A \rangle (\zeta_{hA}(t) - \zeta_{hB}(t)) - \sum_m \langle \delta X \delta s_m \rangle \cdot \nabla \gamma_m(t) \quad (3.19)$$

where

$$\mathbf{s}_m(\Gamma) = \int d\mathbf{r} (\mathbf{r} - \mathbf{r}_0) A_m(\Gamma, \mathbf{r}) \quad (3.20)$$

and for any phase function  $X(\Gamma)$  we define

$$\delta X(\Gamma) = X(\Gamma) - \langle X \rangle. \quad (3.21)$$

Here  $\langle \dots \rangle$  denotes an average over the equilibrium canonical ensemble distribution,

$$f_e(\Gamma) = \exp[-\beta H(\Gamma)] / Q \quad (3.22)$$

and  $Q$  is defined by the normalization of  $f_e$  to unity. We introduce here the convention of writing

$$X(\Gamma) = \int d\mathbf{r} X(\Gamma, \mathbf{r}) \quad (3.23)$$

for any density  $X(\Gamma, \mathbf{r})$  integrated over  $\mathbf{r}$ . Densities are always written with an explicit  $\mathbf{r}$  argument.

### 3.3. Non-equilibrium distribution function

We begin by writing the exact distribution function as a sum

$$f(\Gamma, t) = f_0(\Gamma, t) + f^*(\Gamma, t) \quad (3.24)$$

where  $f^*$  is zero at  $t = 0$  and is defined by this equation at later times. Averages over  $f$  will be written in a similar way as

$$\overline{X(t)} = \langle X \rangle_{0t} + \overline{X^*(t)} \quad (3.25)$$

where the term coming from the average over  $f^*$  is often called the irreversible part [19]. By substitution of (3.24) into the Liouville equation and then solving for  $f^*$  we obtain

$$f^*(\Gamma, t) = - \int_0^t e^{-iL(t-s)} \left( \frac{\partial}{\partial s} + iL \right) f_0(\Gamma, s). \quad (3.26)$$

When the indicated operations are carried out the result is

$$f^*(\Gamma, t) = \int_0^t ds e^{-iL(t-s)} f_0(\Gamma, s) \sum_m \int d\mathbf{r} \{ \delta_{0s} \dot{A}_m(\Gamma, \mathbf{r}) \gamma_m(\mathbf{r}, s) + \delta_{0s} A_m(\Gamma, \mathbf{r}) \dot{\gamma}_m(\mathbf{r}, s) \} \quad (3.27)$$

where, for deviations from the local equilibrium average at time  $t$ , we use the notation

$$\delta_{0t} X(\Gamma) = X(\Gamma) - \langle X \rangle_{0t}. \quad (3.28)$$

In equation (3.27)  $\delta_{0s} \dot{A}_m$  replaces  $\dot{A}_m$  in the as-derived result by virtue of equation (A.1) of the appendix with  $X = 1$ .

A more convenient form of  $f^*$  for calculating transport coefficients is one which contains the thermodynamic forces of the model ( $\nabla \gamma_m$  and  $[\zeta_{hA} - \zeta_{hB}]$ ) rather than the thermodynamic functions  $\gamma_m$  and their time derivatives. To obtain this we first note that the result of taking the time derivative of  $A_m$  can be written in the form of a conservation equation,

$$\dot{A}_m(\Gamma, \mathbf{r}) = -\nabla \cdot \mathbf{J}_m(\Gamma, \mathbf{r}) + J_{\text{tm}}(\Gamma, \mathbf{r}) \quad (3.29)$$

where, corresponding to equation (3.7), we use the notations

$$\mathbf{J}_m = \{ \mathbf{J}_H, \{ \mathbf{P}_\alpha \}, \{ \mathbf{J}_a \}, \mathbf{J}_{hA}, \mathbf{J}_{hB} \} \quad (3.30)$$

$$J_{\text{tm}} = \{ 0, 0, 0, -J_r, J_r \}. \quad (3.31)$$

For those densities  $A_m$  for which  $J_{\text{tm}}$  is here defined as zero, the expressions for the flux densities  $J_m$  are derived and summarized in, for example, ch 8 of [19]. (These are the flux  $\mathbf{J}_H$  of energy, the component  $\mathbf{P}_\alpha$  ( $\equiv \mathbf{P} \cdot \mathbf{e}_\alpha$  where  $\mathbf{e}_\alpha$  is a unit vector in direction  $\alpha$ ) of the pressure tensor  $\mathbf{P}$  and the flux  $\mathbf{J}_a$  of  $a$  atoms.) For the other densities, which refer to the hopping atom, differentiation of the density, equation (3.12), with respect to  $t$  and a property of the delta function yield

$$\mathbf{J}_{hi}(\Gamma, \mathbf{r}) = \delta(\mathbf{r} - \mathbf{r}_h) \theta_i(\Gamma) \mathbf{p}_h / m_h \quad i = A, B \quad (3.32)$$

$$J_r(\Gamma, \mathbf{r}) = -\delta(\mathbf{r} - \mathbf{r}_h) \dot{\theta}_A(\Gamma) = \delta(\mathbf{r} - \mathbf{r}_h) \dot{\theta}_B(\Gamma). \quad (3.33)$$

The quantity  $J_r$  is the *reactive* flux associated with the activated hops between the two wells. When equation (3.29) is used to eliminate  $\dot{A}_m$  from the first sum in equation (3.27) and an integration by parts over  $\mathbf{r}$  is made on the terms containing  $-\nabla \cdot \mathbf{J}_m$  then that sum takes the desired form:

$$\int d\mathbf{r} \sum_m \delta_{0s} \dot{A}_m(\Gamma, \mathbf{r}) \gamma_m(\mathbf{r}, s) = \int d\mathbf{r} \left\{ \delta_{0s} J_r(\Gamma, \mathbf{r}) [\zeta_{hA}(\mathbf{r}, s) - \zeta_{hB}(\mathbf{r}, s)] + \sum_m \delta_{0s} \mathbf{J}_m(\Gamma, \mathbf{r}) \cdot \nabla \gamma_m(\mathbf{r}, s) \right\}. \quad (3.34)$$

A somewhat similar form can be found for the second sum in (3.27). Here we must first eliminate  $\dot{\gamma}_m$  by using an identity, equation (A.5), derived in the appendix:

$$\dot{\gamma}_m(\mathbf{r}, t) = - \sum_n \int d\mathbf{r}' G_{mn,0t}^{-1}(\mathbf{r}, \mathbf{r}') (\langle \dot{A}_n(\mathbf{r}') \rangle_{0t} + \overline{\dot{A}_n^*(\mathbf{r}', t)}) \quad (3.35)$$

where the functions  $G$  are defined by the equation

$$G_{mn,0t}(\mathbf{r}, \mathbf{r}') = \langle \delta_{0t} A_m(\mathbf{r}) \delta_{0t} A_n(\mathbf{r}') \rangle_{0t} \quad (3.36)$$

and inverse functions  $G^{-1}$  are then defined by the equation

$$\delta_{mn} \delta(\mathbf{r} - \mathbf{r}') = \sum_p \int d\mathbf{r}'' G_{mp,0t}^{-1}(\mathbf{r}, \mathbf{r}'') G_{pn,0t}(\mathbf{r}'', \mathbf{r}'). \quad (3.37)$$

An identity, equation (A.2), derived in the appendix allows the local equilibrium average of  $\dot{A}_n$  appearing in equation (3.35) to be related to the thermodynamic forces:

$$\langle \dot{A}_n(\mathbf{r}') \rangle_{0t} = \int d\mathbf{r}'' \left\{ \langle \delta_{0t} A_n(\mathbf{r}') \delta_{0t} J_r(\mathbf{r}'') \rangle_{0t} [\zeta_{hA}(\mathbf{r}'', t) - \zeta_{hB}(\mathbf{r}'', t)] + \sum_p \langle \delta_{0t} A_n(\mathbf{r}') \delta_{0t} \mathbf{J}_p(\mathbf{r}'') \rangle_{0t} \cdot \nabla_{r''} \gamma_p(\mathbf{r}'', t) \right\}. \quad (3.38)$$

When equation (3.35) (with the local equilibrium average terms substituted from equation (3.38)) is used to eliminate  $\dot{\gamma}_m$  from the second sum in equation (3.27) each term in the result contains some terms in which the thermodynamic forces appear explicitly and others in which the irreversible parts  $\overline{\dot{A}_n^*}$  appear. This lengthy expression, plus that in equation (3.34), can be used to rewrite the earlier expression for the distribution function, equations (3.24) and (3.27), as

$$f(\Gamma, t) = f_0(\Gamma, t) + \int_0^t ds e^{-iL(t-s)} f_0(\Gamma, s) \int d\mathbf{r} \left\{ \delta_{0s} \hat{J}_r(\Gamma, \mathbf{r}, s) [\zeta_{hA}(\mathbf{r}, s) - \zeta_{hB}(\mathbf{r}, s)] + \sum_m \left( \delta_{0s} \hat{\mathbf{J}}_m(\Gamma, \mathbf{r}, s) \cdot \nabla \gamma_m(\mathbf{r}, s) - N_{m,0s}(\Gamma, \mathbf{r}) \overline{\dot{A}_m^*(\mathbf{r}, s)} \right) \right\} \quad (3.39)$$

where

$$N_{m,0t}(\Gamma, \mathbf{r}) = \sum_n \int d\mathbf{r}' \delta_{0t} A_n(\Gamma, \mathbf{r}') G_{nm,0t}^{-1}(\mathbf{r}', \mathbf{r}) \quad (3.40)$$

$$\hat{\phi}(\Gamma, \mathbf{r}, t) = \phi(\Gamma, \mathbf{r}) - \sum_{n,p} \int d\mathbf{r}' \int d\mathbf{r}'' \delta_{0t} A_n(\Gamma, \mathbf{r}') G_{np,0t}^{-1}(\mathbf{r}', \mathbf{r}'') \langle \delta_{0t} A_p(\mathbf{r}'') \phi(\mathbf{r}') \rangle_{0t} \quad (3.41)$$

$\phi = \mathbf{J}_m, J_r$ .

For each flux,  $\phi$ , appearing in the conservation equations, equation (3.41) defines a corresponding *subtracted* flux,  $\hat{\phi}$ . The relationship between the corresponding fluctuations,

$\delta_{0t}\phi(\Gamma, \mathbf{r})$  and  $\delta_{0t}\hat{\phi}(\Gamma, \mathbf{r}, t)$  defined in (3.28), is just equation (3.41) with the symbols  $\phi$  and  $\hat{\phi}$  everywhere replaced by  $\delta_{0t}\phi$  and  $\delta_{0t}\hat{\phi}$ , respectively. In the absence of the hopping atom, and hence of the reactive fluxes, (3.41) is equivalent to equation (25) of [23]. It will be convenient to delay further comment on the role of the subtracted fluxes to the next section.

### 3.4. Irreversible parts of fluxes and the kinetic equation

According to equation (3.25) each flux is the sum of a local equilibrium part and an irreversible part. The former is the convective contribution associated with the centre of mass motion of the system relative to the fixed external axes used in defining the fluxes. As outlined in appendix A.2 these convective parts make no contribution to the entropy production, which is found to be the spatial integral of a sum of products of the irreversible fluxes and the thermodynamic forces:

$$\dot{S} = k \int d\mathbf{r} \left\{ \overline{J_r^*}(\mathbf{r})[\zeta_{hA}(\mathbf{r}) - \zeta_{hB}(\mathbf{r})] + \sum_m \overline{J_m^*}(\mathbf{r}) \cdot \nabla \gamma_m(\mathbf{r}) \right\}. \quad (3.42)$$

For a system with a linear temperature gradient and non-equilibrium occupancies of sites  $A$  and  $B$  but with no other thermodynamic forces this becomes, in the limit  $v = 0$  and correct to first order in deviations from equilibrium,

$$T\dot{S} = \overline{J_q^*} \cdot \mathbf{X}_q + \overline{J_r^*} X_r \quad (3.43)$$

where the thermodynamic forces are here defined by

$$\mathbf{X}_q = -\nabla T/T \quad X_r = -[\mu_{hB} - \mu_{hA}] \quad (3.44)$$

and where

$$\mathbf{J}_q(\Gamma) = \mathbf{J}_H(\Gamma) - \sum_b h_b \mathbf{J}_b(\Gamma) - (h_{hA} - h_{hB})(\mathbf{r}_h - \mathbf{r}_0)\dot{\theta}_A(\Gamma). \quad (3.45)$$

Thus  $\mathbf{J}_q$  can be identified as the microscopic expression for the heat flux in this system. In deriving equation (3.43) it must be noted that the gradient of  $\zeta_b = \beta\mu_b$  contains a contribution from the temperature gradient since

$$\nabla(\beta\mu_b) = \beta\nabla_T\mu_b + h_b\nabla\beta \quad (3.46)$$

where  $\nabla_T$  is the spatial derivative taken with  $T$  constant and  $h_b$  is the partial molecular enthalpy of species  $b$ . Here and subsequently  $b = a, hA, hB$ .

Turning to the actual evaluation of the irreversible fluxes, we first obtain

$$\overline{\phi^*(\mathbf{r}, t)} = \overline{\delta_{0t}\phi(\mathbf{r})} = \overline{\delta_{0t}\hat{\phi}(\mathbf{r}, t)} \quad (3.47)$$

by using equations (3.25) and (3.28) for the first equality and (3.41) and (3.14) for the second. The irreversible part of the flux can therefore be calculated as the average of the fluctuation of the subtracted flux. Using equation (3.39), we then obtain

$$\begin{aligned} \overline{\phi^*(\mathbf{r}, t)} = \int_0^t ds \int d\mathbf{r}' \left\{ \langle [e^{iL(t-s)} \delta_{0t}\hat{\phi}(\mathbf{r}, t)] \delta_{0s} \hat{J}_r(\mathbf{r}', s) \rangle_{0s} (\zeta_{hA}(\mathbf{r}', s) - \zeta_{hB}(\mathbf{r}', s)) \right. \\ \left. + \sum_n \langle [e^{iL(t-s)} \delta_{0t}\hat{\phi}(\mathbf{r}, t)] \delta_{0s} \hat{J}_n(\mathbf{r}', s) \rangle_{0s} \cdot \nabla_{r'} \gamma_n(\mathbf{r}', s) + R^*(\mathbf{r}, \mathbf{r}', t, s) \right\} \quad (3.48) \end{aligned}$$

$$\phi = \mathbf{J}_m, J_r$$

where

$$R^*(\mathbf{r}, \mathbf{r}', t, s) = \sum_n \langle [e^{iL(t-s)} \delta_{0t}\hat{\phi}(\mathbf{r}, t)] N_{n,0s}(\mathbf{r}') \rangle_{0s} \left\{ \nabla_{r'} \cdot \overline{J_n^*}(\mathbf{r}', s) - \overline{J_m^*}(\mathbf{r}', s) \right\}. \quad (3.49)$$

The Liouville operator acts only inside the square brackets.

Equation (3.48) provides a set of exact nonlinear equations for the fluxes which are similar to equations of Wong *et al* [23] and Ramshaw [24] but contain reactive flux terms. To extract useful approximate results some systematic expansion method is needed, as discussed in these papers in the context of the transport properties of fluids. A simple procedure, sometimes called [24] a naive Chapman–Enskog expansion in the fluid case, is to write the fluxes as  $\bar{\phi} = \langle \phi \rangle_0 + \lambda \bar{\phi}^*$  where  $\lambda$  is a ‘small’ parameter, and make an iterative solution. The zeroth approximation is therefore  $\langle \phi \rangle_0$  and the first approximation adds to this  $\bar{\phi}^*$  calculated from (3.48) with the irreversible parts of the fluxes set to zero, i.e.  $R^* = 0$  in (3.48). We shall use this first approximation combined with two physical assumptions. First, we restrict consideration to first-order deviations from thermodynamic equilibrium and to linear gradients of the thermodynamic functions  $\gamma_m$ . The averages over the local equilibrium distribution function in the TCFs appearing in (3.48) can therefore be replaced by equilibrium averages. This replacement implies we have also taken the limit  $v = 0$ , as is required since the TCFs are later associated with jump frequencies, which are by definition independent of the mean centre of mass velocity. Second, it will be assumed that there is a range of times  $\tau$  for which these TCFs have decayed essentially to zero and that changes of the thermodynamic functions and forces in the time 0 to  $\tau$  are negligible. This is the  $\tau$  timescale introduced in equation (2.5), which comprises times longer than the characteristic microscopic relaxation time,  $\tau_r$ , sufficient for the TCFs to decay to zero and shorter than both the time,  $\tau_e$ , for appreciable change in the populations of sites  $A$  and  $B$  and also the longer time for change in bulk thermodynamic properties.

The kinetic equation we seek is obtained by introducing these assumptions and approximations into equation (3.48), putting  $\phi = -J_r$  and integrating over  $r$ . For comparison with section 2 we further assume that the only deviations from equilibrium arise from a uniform one-dimensional temperature gradient along the  $x$ -axis and from non-equilibrium site occupancies for sites  $A$  and  $B$ . The result is

$$-\overline{J_r(\tau)} \equiv \frac{d\theta_A(\tau)}{d\tau} = \left( \int_0^\tau ds \langle \hat{\theta}_A(s) e_A \cdot \hat{J}_q \rangle \right) \nabla_x \beta - \left( \int_0^\tau ds \langle \hat{\theta}_A(s) \hat{\theta}_A \rangle \right) [\zeta_{hA} - \zeta_{hB}] \quad (3.50)$$

where  $e_A$  is a unit vector along the  $x$ -axis in the direction from site  $A$  to  $B$  and the  $t = 0$  arguments on the thermodynamic functions have been dropped. Advantage has been taken of the fact that, to first order in deviations from equilibrium,  $\langle \hat{\theta}_A \rangle_{0t} = 0$ , as follows from equation (3.19) and the expectation that  $\hat{\theta}_A$  is an odd function of momenta. It is shown in appendix A.3 that the definitions of the subtracted fluxes appearing here reduce to

$$\hat{\phi}(\Gamma) = \phi(\Gamma) - \beta \int d\mathbf{r} \mathbf{g}(\Gamma, \mathbf{r}) \cdot \langle \mathbf{g}(\mathbf{r}) \phi \rangle \langle \rho(\mathbf{r}) \rangle^{-1} \quad \phi = \hat{\theta}_A, \mathbf{J}_q \quad (3.51)$$

where  $\langle \rho(\mathbf{r}) \rangle$  is the mean mass density at  $\mathbf{r}$ .

The approximations introduced after equation (3.49) are similar to those made in older derivations of the Green–Kubo expressions for transport coefficients of chemically inert fluids [25]. The simple expansion procedures in those theories were subsequently realized to be unsatisfactory because of inconsistencies in treating macroscopic and microscopic dynamics at each level of approximation ([24, 26] and references therein). However, for the fluid case the set of densities  $A_m$  is restricted to the densities of energy, of linear momentum and of the number of each chemical species; the spatial integral of each density is conserved. These densities (or rather their Fourier transforms) can then be designated as ‘slow’ variables and more satisfactory systematic expansion procedures can be introduced, see [24, 26, 27]. In the present model the spatial integrals of the additional densities,  $n_{hA}$  and  $n_{hB}$ , associated with

the reactive fluxes are not conserved quantities. Fortunately these densities can plausibly be considered as slow variables like the others if the activation energy,  $\Delta g$ , for each jump is large compared with  $kT$  so that the rate of atom exchange between the two sites  $A$  and  $B$  is very small. Indeed, Chandler [10], working in a different formal framework and considering an isothermal system without macroscopic gradients, identified  $\exp(-\Delta g/kT)$  as an expansion parameter for the dynamical model. However, the development of a systematic expansion for our model, for example along the general lines suggested in [24], seems not trivial and is not attempted here.

The kinetic equation (3.50) and results derived from it, like the expressions for the transport coefficients of chemically inert fluids [19], contain TCFs of subtracted fluxes  $\hat{\phi}$  rather than of the fluxes  $\phi$  introduced through conservation equations. This comes as an automatic consequence of retaining *all* contributions in the distribution function (3.39) that are linear in the thermodynamic forces. In fact subtracted fluxes have two properties, following from their definition (3.41), which are usually found and believed necessary [27, 28] for fluxes appearing in TCFs associated with transport coefficients. They are orthogonal to fluctuations in the densities of conserved quantities, i.e.  $\langle \hat{\phi} \delta A_m(\mathbf{r}) \rangle = 0$ , and are of the form  $\hat{\phi} = (1 - P)\phi$  where  $P$  is a projection operator linear in the fluctuations  $\delta A_m(\mathbf{r})$ . The main point is that the time integral from 0 to  $\infty$  of  $\langle \phi \phi(t) \rangle$  diverges if  $\phi$  has a conserved part but it is a reasonable assumption that  $\langle \hat{\phi} \hat{\phi}(t) \rangle$  does not [27]. Whether the difference between having  $\hat{\phi}$  or  $\phi$  is of practical significance has to be determined for the particular TCF expression of interest. (An example is provided by the tracer and collective diffusion coefficients of fluids. There each  $\phi$  is the sum of appropriate atom velocities and the corresponding  $\hat{\phi}$  is constructed from it by subtracting the velocity of the centre of mass from each atom velocity. The difference between having  $\hat{\phi}$  or  $\phi$  is found [28] to be negligible for the tracer but not for a collective diffusion coefficient.)

## 4. Results and discussion

### 4.1. Expressions for the jump frequency and the heat of transport

It is clear that before equation (3.50) can be compared with the phenomenological theory, equation (2.7), the thermodynamic force ( $\zeta_A - \zeta_B$ ) must be expressed in terms of  $\Delta\theta_A(0)$ . The relation needed is found from equation (3.19) to be

$$\zeta_{hA} - \zeta_{hB} = \frac{\Delta\theta_A(0)}{\langle (\delta\theta_A)^2 \rangle} + \frac{\langle \delta\theta_A \mathbf{e}_A \cdot \delta \mathbf{s} \rangle}{\langle (\delta\theta_A)^2 \rangle} \nabla_x \beta \quad (4.1)$$

where

$$\mathbf{s}(\Gamma) = \int d\mathbf{r} (\mathbf{r} - \mathbf{r}_0) \left\{ H(\Gamma, \mathbf{r}) - \sum_b n_b(\Gamma, \mathbf{r}) h_b \right\}. \quad (4.2)$$

Comparison of the two equations then yields expressions for the isothermal jump frequencies and the sum of the reduced heats of transport as canonical ensemble averages:

$$\lambda = w_\alpha / \langle \theta_B \rangle = w_\beta / \langle \theta_A \rangle = \frac{\int_0^\tau dt \langle \hat{\theta}_A(t) \hat{\theta}_A \rangle}{\langle (\delta\theta_A)^2 \rangle} \quad (4.3)$$

$$q_\alpha^* + q_\beta^* = -\frac{2}{a} \frac{\int_0^\tau dt \langle \hat{\theta}_A \mathbf{e}_A \cdot \hat{\mathbf{J}}_q(t) \rangle}{w_\alpha \langle \theta_A \rangle} + 2h^* \quad (4.4)$$

where

$$h^* = \frac{1}{a} \left[ \frac{\langle \theta_A \mathbf{s} \cdot \mathbf{e}_A \rangle}{\langle \theta_A \rangle} - \frac{\langle \theta_B \mathbf{s} \cdot \mathbf{e}_A \rangle}{\langle \theta_B \rangle} \right]. \quad (4.5)$$

The stationary and time reversal symmetry properties of the TCFs [29] have been used to obtain the form in equation (4.4).

Equation (4.4) gives only the sum of the two reduced heats of transport for jumps in the two directions between sites  $A$  and  $B$ . This is not necessarily important since the exact expressions [17] for the phenomenological coefficients contain only such sums. Nevertheless, in order to make contact with earlier work, it is worth trying to resolve the expression into two terms which can be assigned to the individual jumps. To do this we first define  $\theta(\xi)$  as the Heaviside step function, which is unity for  $\xi > 0$  and is zero for  $\xi < 0$ . By substituting the identity  $\theta(\xi) + \theta(-\xi) = 1$  and using equation (3.2) one can then write the TCF of equation (4.4) as

$$-\langle \hat{\theta}_A e_A \cdot \hat{\mathbf{J}}_q(t) \rangle = \langle \hat{\theta}_B \theta(\xi) e_A \cdot \hat{\mathbf{J}}_q(t) \rangle + \langle \hat{\theta}_A \theta(-\xi) e_B \cdot \hat{\mathbf{J}}_q(t) \rangle \quad (4.6)$$

where  $e_B = -e_A$  is a unit vector along the  $x$ -axis in the direction from site  $B$  to site  $A$ . We associate the first contribution with the  $\alpha$  jump and the second with the  $\beta$  jump. We also associate half of the second term in equation (4.4) with the  $\alpha$  jump and half with the  $\beta$  jump. We can then write

$$q_\alpha^* = \frac{2}{a} \frac{\int_0^\tau dt \langle \hat{\theta}_B \theta(\xi) e_A \cdot \hat{\mathbf{J}}_q(t) \rangle}{w_\alpha \langle \theta_A \rangle} + h^*. \quad (4.7)$$

The expression for  $q_\beta^*$  needed to regain equation (4.4) can, as expected, be obtained from that for  $q_\alpha^*$  by replacing  $\alpha$  by  $\beta$ , interchanging the labels  $A$  and  $B$  and replacing  $\theta(\xi)$  by  $\theta(-\xi)$ .

#### 4.2. Discussion of isothermal jump frequency and heat of transport

An examination in appendix A.4 of the isothermal jump frequency formula, equation (4.3), shows that, for activation energy barriers large compared with  $kT$ , the subtracted flux  $\hat{\theta}_A$  can be replaced by  $\hat{\theta}_A$ . It is then straightforward to see that this expression is the same as that often previously obtained in various equivalent forms for an isothermal activated process (see for example [14] and references therein) by using Onsager's regression of fluctuations hypothesis rather than as here, employing an explicit non-equilibrium distribution function. The structure of this result has been discussed [10, 12] and it has been shown that in the limit  $\tau \rightarrow 0_+$  it reduces to the transition state theory expression for a jump frequency,

$$w_\alpha(\text{TST}) = \frac{\langle \delta(\xi) \xi \theta(\xi) \rangle}{\langle \theta_A \rangle} = \frac{\langle \delta(\xi) \rangle \langle \xi \theta(\xi) \rangle}{\langle \theta_A \rangle}. \quad (4.8)$$

The exact expression for the jump frequency can then be written in a form we shall need below as

$$w_\alpha = w_\alpha(\text{TST}) \kappa_\alpha \quad (4.9)$$

where the transmission coefficient  $\kappa_\alpha$  defined by this equation can be determined by simulation, see for example [8, 12].

When discussing the expression (4.7) for the reduced heat of transport we shall for simplicity consider only the form obtained from it for use in molecular dynamics simulations. In that case averages are taken over a restricted microcanonical ensemble in which the total energy is kept constant and the total linear momentum is kept zero. The relation between the TCF of two fluctuations in different ensembles is independent of  $t$  but care is needed because the differences among averages in the different ensembles ('ensemble corrections') are in general of the same order in the number of particles as the TCF itself [30–32]. The detailed relation between canonical ensemble and molecular dynamics ensemble averages has

been established by Wallace and Straube [31]. Applying equation (39) of their development to equation (4.7) we find the ensemble correction is zero and obtain

$$q_\alpha^* = \frac{2}{a} \frac{\int_0^\tau dt \langle \dot{\theta}_B \theta(\dot{\xi}) e_A \cdot \mathbf{J}_q(t) \rangle'}{w_\alpha \langle \theta_A \rangle} + h^* \quad (4.10)$$

where  $\langle \dots \rangle'$  denotes an average in the molecular dynamics ensemble.

To compare this result with that of Gillan [3] we specialize the discussion to the case of self-diffusion in a one-component crystal considered explicitly by him. His expression for the reduced heat of transport,  $q_G^*$ , of an atom jumping from site  $A$ , the negative of the heat of transport of the vacancy used by him, can be written

$$q_G^* = \frac{2}{a} \frac{\int_0^\tau dt \langle \delta(\xi) \dot{\xi} \theta(\dot{\xi}) e_A \cdot \mathbf{J}_H(t) \theta_B(\tau) \rangle'}{\langle \delta(\xi) \rangle \langle \dot{\xi} \theta(\dot{\xi}) \rangle} + h_v + h_{\text{at}} \quad (4.11)$$

where  $h_v$  is the enthalpy of formation of one vacancy and  $h_{\text{at}}$  is the enthalpy of one atom. The last term is a correction to the original result introduced by Jones *et al* [6]. The time correlation part is more explicit than that in Gillan [3] but is equivalent to the procedure followed in using his result for simulations by Jones *et al* [6], see also [33]. There the mean of the energy flux  $\mathbf{J}_H \cdot e_A$  in the direction of the jump is calculated for various times  $t \geq 0$  using initial configurations sampled from  $\delta(\xi) \exp(-\beta U)$  and initial velocities from  $\dot{\xi} \theta(\dot{\xi}) \exp(-\beta K)$ , where  $U$  and  $K$  denote the system potential and kinetic energy, respectively. This flux decays to zero in 10–20 ps. The function  $\theta_B(\tau)$  has been included in equation (4.11) because, in practice, trajectories of unsuccessful jumps, in which the atom returns from  $B$  to  $A$  before the end of the simulation, are rejected. For comparison, our expression in equation (4.10) reduces, with the aid of equations (4.8) and (4.9) and the identity  $\dot{\theta}_B = \delta(\xi) \dot{\xi}$ , to

$$q^* = \frac{2}{a} \frac{\int_0^\tau dt \langle \delta(\xi) \dot{\xi} \theta(\dot{\xi}) e_A \cdot \mathbf{J}_H(t) \rangle'}{\langle \delta(\xi) \rangle \langle \dot{\xi} \theta(\dot{\xi}) \rangle \kappa} + h^* \quad (4.12)$$

where we have dropped the  $\alpha$  label assuming that, as in the argon simulations, all jumps are of the same type.

The TCF term in (4.12) differs from that in (4.11) both because the unsuccessful jumps are not rejected and because the transmission coefficient for the isothermal jump must also be calculated. If there are no unsuccessful jumps the two TCFs are the same. In practice, the fraction of unsuccessful jumps found in simulations [6] of the heat of transport in argon at 30 K is quite small (about 7%). It does not seem easy to gauge without actual simulations the character of the discrepancies between these two TCF expressions when there is a large fraction of unsuccessful jumps. The remaining contributions in equations (4.11) and (4.12) are  $(h_v + h_{\text{at}})$  and  $h^*$ , respectively. It is shown in appendix A.5 that, for the present model,  $h^* = (h_v + h_{\text{at}})$  for a static lattice model but if lattice vibrations are included then a simple interpretation of  $h^*$  seems to be lacking. The difference between  $h^*$  and  $(h_v + h_{\text{at}})$  will presumably be small for argon.

### 4.3. Onsager reciprocal relation

The kinetic equation, (3.50), from which we inferred the expression for the heat of transport defined in section 2 has the form expected from the entropy production (equation (3.43) with the temperature gradient restricted to the  $x$ -axis):

$$\overline{J_r^*} = L_{rr} X_r + L_{rq} X_q. \quad (4.13)$$

Expressions for the phenomenological coefficients can be written by comparison with equation (3.50). Analogous to the derivation of equation (3.50), the mean heat flux along

the  $x$ -axis on the  $\tau$  timescale can be calculated from the same distribution function (3.48) with the same approximations. The result has the form

$$\overline{J}_q^* = L_{qq} X_q + L_{qr} X_r \quad (4.14)$$

and it is found that  $L_{qr} = L_{rq}$ , thus verifying an Onsager reciprocal relation in this context.

In an isothermal system the heat flux along the  $x$ -axis is  $\overline{J}_q^* = (L_{qr}/L_{rr})\overline{J}_r^*$  and use of the results for the phenomenological coefficients then shows that  $(q_\alpha^* + q_\beta^* - 2h^*)/2$ , the TCF part of the expression (4.4) for  $(q_\alpha^* + q_\beta^*)/2$ , is the coefficient of proportionality between the heat flux  $\overline{J}_q$  and the net matter flux, here defined as  $a\overline{J}_r^* = -a d\overline{\theta}_A^*/d\tau$ , between the two sites. The analogue in Gillan's theory is that  $(q_G^* - h_v - h_{at})$ , the TCF part of his reduced heat of transport  $q_G^*$ , is the mean heat flux per atom jump.

## 5. Conclusion

The approach to the heat of transport in this paper improves on earlier work [3] in three main respects: (i) an explicit non-equilibrium distribution function is used; (ii) an expression for the jump frequency in a non-isothermal system is calculated as well as the heat flow in an isothermal system; (iii) in the limit of a uniform isothermal system the standard expression for jump frequency, previously obtained from the Onsager hypothesis about regression of fluctuations, is reproduced.

An expression, equation (4.4), was found for the sum of the two reduced heats of transport associated with atom–vacancy exchanges between a pair of sites. This was plausibly resolved into an expression, equation (4.7), for the reduced heat of transport associated with one atom jump. In the case of self-diffusion, the latter can be compared with an earlier expression due to Gillan [3]. The TCF parts of the two expressions differ in their treatments of unsuccessful jumps and, additionally, because the new expression contains the transmission coefficient of the isothermal jump. These differences are negligible when the fraction of unsuccessful jumps is very small but are difficult to estimate in other circumstances except by simulation. Our reduced heat of transport also contains an equilibrium part  $h^*$  where the earlier formulation had  $(h_v + h_{at})$ , the sum of the enthalpy of formation of one vacancy plus the enthalpy of one atom. The practical difference between these equilibrium parts is probably often small since  $h^* = (h_v + h_{at})$  in a static-lattice approximation.

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## Appendix

### A.1. Identities associated with the nonequilibrium ensemble

There are two useful identities for the local equilibrium average of the time derivative of some variable  $X$ . The first of these,

$$\langle \dot{X} \rangle_{0r} = \int dr \sum_n \langle X \dot{A}_n(r) \rangle_{0r} \gamma_n(r, t) \quad (A.1)$$

can be obtained by shifting the Liouville operator in  $\dot{X} = iLX$  from  $X$  to  $f_{0t}$  and using equation (3.15).

Equation (A.1) can also be written in an alternative form in which  $X$  and  $\dot{A}_n$  are replaced by their fluctuations,  $\delta_{0t}X$  and  $\delta_{0t}\dot{A}_n(\mathbf{r})$ , since all the additional terms vanish by application of (A.1) with  $X = 1$ . Substitution for  $\dot{A}_n$  from the conservation equation (3.28) into this alternative form and integration by parts over  $\mathbf{r}$  in the terms containing  $-\nabla \cdot \mathbf{J}_n$  leads to an expression containing the thermodynamic forces:

$$\langle \dot{X} \rangle_{0t} = \int d\mathbf{r} \left\{ \langle \delta_{0t}X \delta_{0t} \mathbf{J}_r(\mathbf{r}) \rangle_{0t} [\zeta_{hA}(\mathbf{r}, t) - \zeta_{hB}(\mathbf{r}, t)] + \sum_n \langle \delta_{0t}X \delta_{0t} \mathbf{J}_n(\mathbf{r}) \rangle_{0t} \cdot \nabla \gamma_n(\mathbf{r}, t) \right\}. \quad (\text{A.2})$$

A useful identity for the time derivative of a local equilibrium average is readily found by carrying out the differentiation using the form in (3.15) for the local equilibrium distribution function:

$$\frac{\partial \langle X \rangle_{0t}}{\partial t} = - \sum_n \int d\mathbf{r} \langle \delta_{0t}X \delta_{0t} A_n(\mathbf{r}) \rangle_{0t} \dot{\gamma}_n(\mathbf{r}, t). \quad (\text{A.3})$$

In the particular case where  $X = A_m(\mathbf{r})$  we then obtain, with the aid of equation (3.14),

$$\frac{\partial \langle A_m(\mathbf{r}) \rangle_{0t}}{\partial t} = \overline{\dot{A}_m(\mathbf{r}, t)} = - \sum_n \int d\mathbf{r}' G_{mn,0t}(\mathbf{r}, \mathbf{r}') \dot{\gamma}_n(\mathbf{r}', t) \quad (\text{A.4})$$

where the  $G$  functions are defined by equation (3.36). This relation may be inverted with the aid of the definition of  $G^{-1}$  functions in equation (3.37) to obtain

$$\dot{\gamma}_m(\mathbf{r}, t) = - \sum_n \int d\mathbf{r}' G_{mn,0t}^{-1}(\mathbf{r}, \mathbf{r}') \overline{\dot{A}_n(\mathbf{r}', t)}. \quad (\text{A.5})$$

### A.2. Entropy production

It follows from the definition in equation (3.13) that the rate of change of entropy is

$$\dot{S}(t) = -k \int d\Gamma \frac{\partial f_0(\Gamma, t)}{\partial t} \ln f_0(\Gamma, t). \quad (\text{A.6})$$

Substitution for the local equilibrium distribution function and some simplification yields

$$\dot{S}(t) = -k \int d\mathbf{r} \sum_m \dot{\gamma}_m(\mathbf{r}, t) \overline{\dot{A}_m(\mathbf{r}, t)} \quad (\text{A.7})$$

where equation (A.4) has been used to introduce  $\overline{\dot{A}_m}$ . When the latter is written as in equation (3.25) as a sum of local equilibrium and irreversible parts it is seen that the local equilibrium parts sum to zero (using equation (A.1) with  $X = 1$ ). By substitution for  $\overline{\dot{A}_m}$  from the conservation equation (3.29) and integration by parts over  $\mathbf{r}$  for the terms containing the divergence of the fluxes  $\mathbf{J}_m$  one then obtains equation (3.42) for the entropy production.

### A.3. The subtracted fluxes in equation (3.51)

The densities  $A_m$ , equation (3.7), are of even parity in momenta except for the momentum density components,  $g_\alpha$ , which are odd. Since the matrix elements  $G_{mn}$ , equation (3.36) with  $0t$  subscripts deleted everywhere, are zero except when  $A_m$  and  $A_n$  have the same parity in momenta it follows that the matrices  $G$  and  $G^{-1}$  have a similar block form, for example

$$G = \begin{bmatrix} G^{(e)} & 0 \\ 0 & G^{(o)} \end{bmatrix} \quad (\text{A.8})$$

where the label e (o) signifies that the elements are constructed from densities that are of even (odd) parity. Turning to equation (3.41) (with  $0t$  labels omitted), we note that  $\langle \delta A_p(\mathbf{r}'') \delta \phi(\mathbf{r}) \rangle$  is non-zero only when  $A_p$  is of odd parity (when we restrict attention to  $\phi = \mathbf{J}_q, \theta_A$ , which are odd). After evaluation of the elements of  $G^{(o)}$  and  $(G^{(o)})^{-1}$  we finally obtain equation (3.51), where  $\langle \rho(\mathbf{r}) \rangle = \sum_b m_b \langle n_b(\mathbf{r}) \rangle$ .

#### A.4. Effect of the distinction between subtracted flux and ordinary flux in the case of the isothermal jump frequency

At  $t = 0$  the TCF appearing in the isothermal jump frequency, equation (4.3), is reduced by substitution of the definition (3.51) for the subtracted flux and some simplification to

$$\langle (\hat{\theta}_A)^2 \rangle = \langle (\dot{\theta}_A)^2 \rangle - \langle (\Delta \dot{\theta}_A)^2 \rangle \quad (\text{A.9})$$

where  $\Delta \dot{\theta}_A$  stands for the second term in (3.51) and

$$\langle (\Delta \dot{\theta}_A)^2 \rangle = \langle \dot{\theta}_A \Delta \dot{\theta}_A \rangle = \beta \int d\mathbf{r} |(\mathbf{g}(\mathbf{r}) \dot{\theta}_A)|^2 \langle \rho(\mathbf{r}) \rangle^{-1}. \quad (\text{A.10})$$

The velocity integrations can be carried out in the two terms on the right of (A.9) if we substitute  $\dot{\theta}_A = -\dot{\xi} \delta(\xi)$  and take an explicit form for the reaction coordinate. Following [6] and [8] we take the latter to have the form

$$\xi = \sum_i' \mathbf{a}_i \cdot \mathbf{r}_i \quad (\text{A.11})$$

where the primed summation is over the hopping atom and a set of its neighbours. Each vector  $\mathbf{a}_i$  is a unit vector in the jump direction multiplied by a weight; the weights are chosen so that

$$\sum_i' |\mathbf{a}_i|^2 = 1 \quad \sum_i' \mathbf{a}_i = 0. \quad (\text{A.12})$$

After carrying out the velocity integrations the first term on the right of (A.9) is then reduced to

$$\langle (\dot{\theta}_A)^2 \rangle = (\beta \mu)^{-1} \langle \delta(\xi) \rangle \quad (\text{A.13})$$

where the reduced mass  $\mu$  is defined by

$$\mu = \left( \sum_i' |\mathbf{a}_i|^2 / m_i \right)^{-1}. \quad (\text{A.14})$$

$\langle \delta(\xi) \rangle$  is the probability that the hopping atom is at the top of the barrier and is therefore proportional to  $\exp(-\Delta g/kT)$ , where  $\Delta g$  is the activation energy barrier. For the second term in (A.9) we find

$$\langle (\Delta \dot{\theta}_A)^2 \rangle = \frac{\langle \delta(\xi) \rangle^2}{\beta} \sum_i' \sum_j' \mathbf{a}_i \cdot \mathbf{a}_j \int d\mathbf{r} \left[ \frac{\langle \delta(\xi) \delta(\mathbf{r} - \mathbf{r}_i) \rangle}{\langle \delta(\xi) \rangle} \right] \left[ \frac{\langle \delta(\xi) \delta(\mathbf{r} - \mathbf{r}_j) \rangle}{\langle \delta(\xi) \rangle} \right] \langle \rho(\mathbf{r}) \rangle^{-1}. \quad (\text{A.15})$$

Each quantity in square brackets is the probability density that the relevant atom ( $i$  or  $j$ ) is at  $\mathbf{r}$  when the reaction coordinate is zero. This probability density for atom  $i$ , for example, will be sharply peaked at some position  $\mathbf{r}_i^*$  close to the position of  $i$  in a static-lattice calculation of the transition state; for order of magnitude purposes we can approximate the probability density as  $\delta(\mathbf{r} - \mathbf{r}_i^*)$ . We then obtain

$$\langle (\Delta \dot{\theta}_A)^2 \rangle = \beta^{-1} \langle \delta(\xi) \rangle^2 \sum_i' |\mathbf{a}_i|^2 \langle \rho(\mathbf{r}_i^*) \rangle^{-1}. \quad (\text{A.16})$$

For the mass density we have

$$\langle \rho(\mathbf{r}_i^*) \rangle = \sum_j m_j \langle \delta(\mathbf{r}_j - \mathbf{r}_i^*) \rangle \approx m_i \quad (\text{A.17})$$

assuming that the relative probability of an atom other than  $i$  being at  $\mathbf{r}_i^*$  is negligible. From equations (A.13), (A.16) and (A.17),  $\langle (\Delta\dot{\theta}_A)^2 \rangle / \langle (\dot{\theta}_A)^2 \rangle$  is therefore of the order of magnitude of  $\langle \delta(\xi) \rangle$ . The difference between using the subtracted flux  $\hat{\theta}_A$  and the flux  $\dot{\theta}_A$  in evaluating the TCF at  $t = 0$  is therefore a term of relative order  $\langle \delta(\xi) \rangle$ , which is negligible for barriers large compared with  $kT$ . We assume that this remains true at later times at which the TCFs differ significantly from zero.

#### A.5. The term $h^*$ in the heat of transport

For the self-diffusion model of section 4.2 the definition of  $h^*$ , equation (4.5), can be written as

$$h^* = \left( (\bar{e} - h_{\text{at}}) \left\langle (\theta_A - \theta_B) \sum_i (\mathbf{r}_i - \mathbf{r}_0) \cdot \mathbf{e}_A \right\rangle + \left\langle (\theta_A - \theta_B) \sum_i (e_i - \bar{e}) (\mathbf{r}_i - \mathbf{r}_0) \cdot \mathbf{e}_A \right\rangle \right) / (a \langle \theta_A \rangle) \quad (\text{A.18})$$

where  $h_{\text{at}}$  is the enthalpy per atom. We now restrict our attention to a static lattice model and choose  $\bar{e}$  as the mean energy per atom of the corresponding perfect crystal, i.e. the crystal with no vacancy. We assume that, as in argon, there is reflection symmetry in the plane passing through  $\mathbf{r}_0$  perpendicularly to the jump vector.

In the second term only atoms close to the vacancy have a non-zero value of  $(e_i - \bar{e})$  in one or both of the initial- and final-state contributions (i.e. when they occur multiplied by either  $\theta_A$  or  $\theta_B$  respectively in equation (A.18)) and hence make a finite contribution in the sum over atoms. Considering the final-state contribution of a particular atom in this sum there is always an atom in the sum which has an initial-state contribution with the same energy  $(e_i - \bar{e})$  but whose position is translated by  $a\mathbf{e}_A$  from the first atom. The second term is therefore  $\sum_i (e_i - \bar{e})$ . A careful examination shows that the first term is  $(h_{\text{at}} - \bar{e})$  and hence that

$$h^* = h_{\text{at}} - \bar{e} + \sum_i (e_i - \bar{e}). \quad (\text{A.19})$$

If a vacancy is formed in a perfect lattice by removing an atom from the bulk to infinity the change in energy is  $-2\bar{e}$  if the other atoms are frozen in position; when they are allowed to relax to new equilibrium positions there is an additional change of energy  $\sum_i (e_i - \bar{e})$ . If the atom is now added back from infinity to the surface there is a further energy change,  $\bar{e}$ . The total energy change when an atom is moved from the bulk to the surface is therefore  $[-\bar{e} + \sum_i (e_i - \bar{e})]$ , and this is the energy of formation of a vacancy in the static lattice model. Hence  $h^* = h_{\text{at}} + h_{\text{v}}$  for the static model.

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