Incoherent Inelastic Neutron Scattering and Self-Diffusion

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The cross section for incoherent inelastic scattering of neutrons by a many-body system is shown to be related to the real part of a generalized self-diffusion coefficient. The latter quantity is defined as the transport coefficient in the extension of Fick's law of diffusion to arbitrary space-time variations of the driving force. The derivation is based on the fluctuation-dissipation theorem, in a form given by Kubo, and on a treatment of conventional self-diffusion due to Montroll. Previous results, given by Vineyard and by Singwi, Sjölander, and Rahman, are shown to be special cases of the present result.

IT has been shown by Van Hove[1] that incoherent inelastic neutron scattering is described by the frequency and wave-vector dependence of the quantity

$$S_i(\boldsymbol{\kappa},\omega)=\frac{1}{2\pi}\int_{-\infty}^{\infty}dt \times e^{-i\omega t}\langle\exp[-i\boldsymbol{\kappa}\cdot\mathbf{R}(0)]\exp[+i\boldsymbol{\kappa}\cdot\mathbf{R}(t)]\rangle. \quad (1)$$

The position of the scattering nucleus at time t is $\mathbf{R}(t)$. The average is taken over a thermal ensemble at temperature T.

The purpose of this note is to point out an exact and remarkably simple relation between $S_i(\boldsymbol{\kappa},\omega)$ and the generalized self-diffusion coefficient $\mathbf{D}(\boldsymbol{\kappa},\omega)$. The latter quantity is defined as the transport coefficient appearing in the generalization of Fick's law of diffusion to arbitrary space-time variations of the driving force,

$$\mathbf{j}(\boldsymbol{\kappa},\omega)=-\mathbf{D}(\boldsymbol{\kappa},\omega)\cdot(\nabla C)_{\kappa,\omega}. \quad (2)$$

Here, $\mathbf{j}(\boldsymbol{\kappa},\omega)$ is the $(\boldsymbol{\kappa},\omega)$th Fourier component of the current density of the diffusing species, as a response to the $(\boldsymbol{\kappa},\omega)$th Fourier component of the gradient ∇C of the concentration of the diffusing species.

It is shown here that the two quantities S_i and $\mathbf{D}$ are related by

$$S_i(\boldsymbol{\kappa},\omega)=[\beta\hbar\omega/\pi\omega^2(1-e^{-\beta\hbar\omega})]\boldsymbol{\kappa}\cdot\mathrm{Re}\mathbf{D}(\boldsymbol{\kappa},\omega)\cdot\boldsymbol{\kappa}. \quad (3)$$

(The abbreviation $\beta=1/kT$ is used.)

The connection between incoherent neutron scattering and self-diffusion has been observed previously. For example, Vineyard[2] derived

$$S_i(\boldsymbol{\kappa},\omega)=\kappa^2D/\pi(\omega^2+\kappa^4D^2) \quad (4)$$

using classical mechanics and an isotropic diffusion model. The quantity D is the self-diffusion coefficient $D(0,0)$ in our notation. It should be noted that Vineyard's calculation did not allow for either frequency dispersion or spatial dispersion of the self-diffusion coefficient. Because of this, one should not place any reliance on the extra κ dependence coming from the denominator of Eq. (4). For small κ, Vineyard's result reduces to

$$S_i(\boldsymbol{\kappa},\omega)\rightarrow\kappa^2D/\pi\omega^2 \quad (5)$$

which is in exact agreement with our Eq. (3) in the limit of small κ and small ω. This is the limit in which one may safely neglect frequency dispersion and spatial dispersion.

In the limit of small κ but arbitrary ω, and for an isotropic medium, Eq. (3) reduces to

$$S_i(\boldsymbol{\kappa},\omega)\rightarrow[\beta\hbar\omega/\pi\omega^2(1-e^{-\beta\hbar\omega})]\kappa^2\,\mathrm{Re}D(0,\omega). \quad (6)$$

This agrees with the result found in the same limit by Singwi, Sjölander, and Rahman,[3] after allowing for differences in notation.

The derivation consists of two parts. First, we use straightforward mathematical manipulations to express $S_i(\boldsymbol{\kappa},\omega)$, as defined by Eq. (1), in terms of a quantity $D_{ab}(\boldsymbol{\kappa},\omega)$, defined by Eq. (14). Then, by an independent argument, we show that $D_{ab}(\boldsymbol{\kappa},\omega)$ is the generalized self-diffusion coefficient.

The derivation of Eq. (3) begins with the observation that

$$\omega^2\int_{-\infty}^{\infty}dt\,e^{-i\omega t}\langle\rho(-\boldsymbol{\kappa},0)\rho(\boldsymbol{\kappa},t)\rangle =\int_{-\infty}^{\infty}dt\,e^{-i\omega t}\langle\dot{\rho}(-\boldsymbol{\kappa},0)\dot{\rho}(\boldsymbol{\kappa},t)\rangle, \quad (7)$$

where

$$\rho(\boldsymbol{\kappa},t)=\exp[i\boldsymbol{\kappa}\cdot\mathbf{R}(t)]. \quad (8)$$

Equation (7) is an identity, provided that the time-correlation function vanishes fast enough as $t\rightarrow\pm\infty$. In the present context there is no reason to doubt that this happens.

Next, we use the further identity

$$\frac{1}{2\pi}\int_{-\infty}^{\infty}dt\,e^{-i\omega t}\langle\dot{\rho}(-\boldsymbol{\kappa},0)\dot{\rho}(\boldsymbol{\kappa},t)\rangle =[\hbar\omega/\pi(1-e^{-\beta\hbar\omega})]\,\mathrm{Re}\sigma(\boldsymbol{\kappa},\omega), \quad (9)$$

[1] L. Van Hove, Phys. Rev. **95**, 249 (1954).
[2] G. H. Vineyard, Phys. Rev. **110**, 999 (1958).
[3] K. S. Singwi, A. Sjölander, and A. Rahman, *Inelastic Scattering of Neutrons in Solids and Liquids* (International Atomic Energy Agency, Vienna, 1963), Vol. I, p. 215.

where the quantity σ is defined by

$$\sigma(\boldsymbol{\kappa},\omega)=\int_0^\infty dt\, e^{-i\omega t}\int_0^\beta d\lambda\langle\dot{\rho}(-\boldsymbol{\kappa},-i\hbar\lambda)\dot{\rho}(\boldsymbol{\kappa},t)\rangle. \quad (10)$$

This identity can be verified easily by expanding in energy eigenstates. It also follows directly from theorems given by Kubo.[4]

Next, we introduce the current-density operator,

$$\mathbf{j}(\boldsymbol{\kappa})=\tfrac{1}{2}[(\mathbf{p}/m)e^{i\boldsymbol{\kappa}\cdot\mathbf{R}}+e^{i\boldsymbol{\kappa}\cdot\mathbf{R}}(\mathbf{p}/m)]. \quad (11)$$

The momentum of the scattering particle is $\mathbf{p}$ and its mass is m. The Heisenberg equation of motion for the density operator $\rho(\boldsymbol{\kappa})$ is just the law of conservation of current density,

$$\dot{\rho}(\boldsymbol{\kappa},t)=i\boldsymbol{\kappa}\cdot\mathbf{j}(\boldsymbol{\kappa},t). \quad (12)$$

Consequently, $\sigma(\boldsymbol{\kappa},\omega)$ may be written as

$$\sigma(\boldsymbol{\kappa},\omega)=\beta\boldsymbol{\kappa}\cdot\mathbf{D}(\boldsymbol{\kappa},\omega)\cdot\boldsymbol{\kappa}. \quad (13)$$

Equation (13) introduces the tensor $\mathbf{D}$; its Cartesian components D_{ab} are given by

$$D_{ab}(\boldsymbol{\kappa},\omega)=\frac{1}{\beta}\int_0^\infty dt\, e^{-i\omega t}\int_0^\beta d\lambda\langle j_b(-\boldsymbol{\kappa},-i\hbar\lambda)j_a(\boldsymbol{\kappa},t)\rangle. \quad (14)$$

The desired Eq. (3) is obtained by combining Eqs. (7), (8), (9), and (13).

The rest of the derivation consists in establishing the connection between $\mathbf{D}(\boldsymbol{\kappa},\omega)$ and self-diffusion. This may be done conveniently by a slight extension of Montroll's calculation[5] of the conventional self-diffusion coefficient, $D(0,0)$ in our notation.

Montroll's procedure is based on the following observation. In linear irreversible thermodynamics, the driving force for self-diffusion, $-kT\nabla C$, and any externally imposed forces $\mathbf{F}$ are additive. Therefore, the self-diffusion coefficient can be found by calculating the response of the system to an external force. The calculation can be performed using Kubo's technique.[4] The interaction of the system with an external field is given by the perturbation Hamiltonian

$$H'=\rho(-\boldsymbol{\kappa})U(\boldsymbol{\kappa},\omega)e^{-i\omega t}. \quad (15)$$

This supposes that the external field U varies as $\exp[i(\boldsymbol{\kappa}\cdot\mathbf{R}-\omega t)]$. The corresponding force is

$$\mathbf{F}(\boldsymbol{\kappa},\omega)=-(\nabla U)_{\kappa,\omega}=i\boldsymbol{\kappa}U(\boldsymbol{\kappa},\omega)e^{-i\omega t}, \quad (16)$$

and the response, according to irreversible thermodynamics, should be written in the form

$$\langle\mathbf{j}(\boldsymbol{\kappa},\omega)\rangle=-\beta\mathbf{D}(\boldsymbol{\kappa},\omega)\cdot\mathbf{F}(\boldsymbol{\kappa},\omega), \quad (17)$$

where $\mathbf{D}(\boldsymbol{\kappa},\omega)$ is the appropriate transport coefficient. Application of Kubo's technique leads to Eq. (14) for the tensor $\mathbf{D}$. Thus it is correct to identify $\mathbf{D}(\boldsymbol{\kappa},\omega)$ with the generalized self-diffusion coefficient.

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[4] R. Kubo, J. Phys. Soc. Japan **12**, 570 (1957).

[5] E. W. Montroll, in *Lectures in Theoretical Physics*, edited by W. E. Brittin, B. W. Downs, and J. Downs (Interscience Publishers, Inc., New York, 1961), Vol. III, p. 261.