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Transport Coefficients of Liquids— Approximate Self-Diffusion Coefficient in a Cell Model

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1. INTRODUCTION

It is well known that transport coefficients may be expressed as integrals of time-correlation functions [1]. However, only very limited calculations of the transport coefficients have been made by this method, referred to as the correlation function method. For dilute gases Mori [2] has given an argument that the correlation function method yields results identical with the Chapman–Enskog theory. In the special case of rigid sphere molecules, Wainwright [3] has shown that the correlation function method is in close agreement with the Enskog dense gas theory, while for real fluids Zwanzig [4] has discovered a method for finding the density expansions of the transport coefficients in which the higher order coefficients involve the solution of difficult many-body molecular problems.

As might be expected, rigorous calculations are virtually impossible for liquids. Because the time-correlation functions are averages over equilibrium ensembles, approaches similar to those used in the calculation of equilibrium properties may be applied in the calculation of transport coefficients. For example, one might use a simplified molecular model, as was done by Longuet–Higgins and Pople [5] for the self-diffusion coefficient of a rigid sphere liquid, or the radial distribution function approach, as was done by Douglass [6], also for self-diffusion. The purpose of this paper is to demonstrate the feasibility of yet another approach, the cell model method.

Even for a cell model the complete time dependence of the correlation functions can be determined only in principle. Therefore, as a matter of expediency, approximations must be introduced in calculation of the transport coefficients. Thus, little theoretical significance may be attached to the results of calculations made in this manner. However, even the simplest form for the self-diffusion time-correlation function consistent with expected behavior yields surprisingly good agreement between the calculated and experimental self-diffusion coefficient of liquid argon at 84° K.

In this paper only the simplest approximation for the cell model self-diffusion coefficient will be discussed in detail. This calculation is given in Section 3, following the development in Section 2 of general relationships for the time-autocorrelation functions. Approaches applicable to the calculation of higher order approximations to the self-diffusion coefficient may also be used for the calculation of viscosity and thermal conductivity coefficients. Some of the problems encountered in the computation of high order approximations are discussed in Section 4.

2. The Autocorrelation Functions

The self-diffusion, viscosity and thermal conductivity time-correlation functions $G_D(t)$, $G_V(t)$, and $G_T(t)$ are related to their corresponding transport coefficients D, η, and K by the formulas

$$\begin{aligned} D &= \frac{1}{3m^2} \int_0^\infty G_D(t)\,dt, \\ \eta &= \frac{1}{VkT} \int_0^\infty G_V(t)\,dt, \\ K &= \frac{1}{VkT^2} \int_0^\infty G_T(t)\,dt, \end{aligned} \tag{2.1}$$

where t is the time, m is the mass per molecule, V is the volume of the system, T is the absolute temperature and k is the Boltzmann constant. Each of the time-correlation functions appearing in Eq. (2.1) may be written in the form

$$G_\alpha(t) = \langle J_\alpha(\{\mathbf{R}(0), \mathbf{P}(0)\})\, J_\alpha(\{\mathbf{R}(t), \mathbf{P}(t)\})\rangle, \tag{2.2}$$

where the generalized index α may be D, V or T. In this expression the generalized dynamical variable $J_\alpha(\{\mathbf{R}(t), \mathbf{P}(t)\})$ is a function of the phase points $\{\mathbf{R}(t), \mathbf{P}(t)\}$ at time t; its specific form is dependent upon the transport coefficient being considered The brackets $\langle\ \rangle$ denote an ensemble average over the initial phase points $\{\mathbf{R}(0), \mathbf{P}(0)\}$ calculated with an equilibrium distribution, which we will take to be the usual canonical distribution in the following development. For notational convenience we will denote $J_\alpha(\{\mathbf{R}(t), \mathbf{P}(t)\})$ by $J_\alpha(t)$ and $J_\alpha(\{\mathbf{R}(0), \mathbf{P}(0)\})$ simply by J_α. Then the time evolution of $J_\alpha(t)$ is given by the dynamical equation

$$\frac{d}{dt} J_\alpha(t) = iLJ_\alpha(t), \tag{2.3}$$

where L is the well-known Liouville operator. We will asume the potential energy U of the system to be of the pairwise additive form

$$U = \frac{1}{2} \sum_{j=1}^{N} \sum_{\substack{k=1 \\ \neq j}}^{N} u_{jk}(R_{jk}), \tag{2.4}$$

where u_{jk} is the mutual potential energy of particles j and k, $R_{jk} = | \mathbf{R}_j - \mathbf{R}_k |$ is their distance of separation and N is the number of particles in the system. For a potential energy of the form of Eq. (2.4) the Liouville operator may be written as

$$L = -i \sum_{j=1}^{N} \mathbf{P}_j \cdot \frac{\partial}{\partial \mathbf{R}_j} - i \sum_{j=1}^{N} \sum_{\substack{k=1 \\ \neq j}}^{N} \mathbf{F}_{jk} \cdot \frac{\partial}{\partial \mathbf{P}_j}, \tag{2.5}$$

where $\mathbf{F}_{jk} = -\partial u_{jk}/\partial \mathbf{R}_j$. The formal solution of Eq. (2.3) is

$$J_\alpha(t) = \sum_{n=0}^{\infty} \frac{t^n}{n!} (iL)^n J_\alpha = \exp(itL) J_\alpha, \tag{2.6}$$

so that Eq. (2.2) for the autocorrelation function may be written in the form

$$G_\alpha(t) = \sum_{n=0}^{\infty} (n!)^{-1} \langle J_\alpha(iL)^n J_\alpha \rangle t^n. \tag{2.7}$$

This expansion reveals the explicit time dependence of the autocorrelation functions. The coefficients $(n!)^{-1} \langle J_\alpha(iL)^n J_\alpha \rangle$ are equilibrium ensemble averages and may therefore be computed, in principle, by the usual statistical mechanical methods. Unfortunately, however, even the lower order coefficients are rather lengthy and, as the order increases, correlations between increasing numbers of particles must be taken into account. We therefore will examine only the lower order coefficients.

Self-Diffusion

For self-diffusion, the dynamical variable of interest J_D is merely the momentum of one of the particles of the system, say particle number one. The self-diffusion autocorrelation function is therefore

$$G_D(t) = \sum_{n=0}^{\infty} (n!)^{-1} \langle J_D(iL)^n J_D \rangle t^n = \sum_{n=0}^{\infty} (n!)^{-1} \langle \mathbf{P}_1 \cdot (iL)^n \mathbf{P}_1 \rangle t^n. \tag{2.8}$$

The odd ordered coefficients in Eq. (2.8) vanish by virtue of the fact that $\langle P_1{}^q \rangle = 0$, if q is an odd integer. The first three even ordered coefficients in Eq. (2.8) are

$$(0!)^{-1} \langle \mathbf{P}_1 \cdot (iL)^0 \mathbf{P}_1 \rangle = \langle \mathbf{P}_1 \cdot \mathbf{P}_1 \rangle, \tag{2.9}$$

$$(2!)^{-1} \langle \mathbf{P}_1 \cdot (iL)^2 \mathbf{P}_1 \rangle = -2 \frac{1}{m} \sum_{j=2}^{N} \left\langle \mathbf{P}_1\mathbf{P}_1 : \frac{\partial^2 u_{1\cdot j}}{\partial \mathbf{R}_1 \, \partial \mathbf{R}_1} \right\rangle, \tag{2.10}$$

$$\begin{aligned}(4!)^{-1} \langle \mathbf{P}_1 \cdot (iL)^4 \mathbf{P}_1 \rangle = \frac{1}{24} \Bigg\{ &- \frac{1}{m^3} \sum_{j=2}^{N} \left\langle \mathbf{P}_1\mathbf{P}_1\mathbf{P}_1\mathbf{P}_1 \vdots \frac{\partial^4 u_{1j}}{\partial \mathbf{R}_1 \, \partial \mathbf{R}_1 \, \partial \mathbf{R}_1 \, \partial \mathbf{R}_1} \right\rangle \\ &- \frac{3}{m^3} \sum_{j=2}^{N} \left\langle \mathbf{P}_j\mathbf{P}_j\mathbf{P}_1\mathbf{P}_1 \vdots \frac{\partial^4 u_{1j}}{\partial \mathbf{R}_j \, \partial \mathbf{R}_j \, \partial \mathbf{R}_1 \, \partial \mathbf{R}_1} \right\rangle \\ &+ \frac{1}{m^2} \sum_{j=2}^{N} \sum_{k \neq j2}^{N} \left\langle \mathbf{P}_1\mathbf{P}_1 : \frac{\partial^2 u_{1j}}{\partial \mathbf{R}_1 \, \partial \mathbf{R}_1} \cdot \frac{\partial^2 u_{1k}}{\partial \mathbf{R}_1 \, \partial \mathbf{R}_1} \right\rangle \\ &+ \frac{3}{m^2} \sum_{j=2}^{N} \sum_{k \neq j2}^{N} \left\langle \mathbf{P}_1\mathbf{P}_1 : \frac{\partial u_{1j}}{\partial \mathbf{R}_1} \cdot \frac{\partial^3 u_{1k}}{\partial \mathbf{R}_1 \, \partial \mathbf{R}_1 \, \partial \mathbf{R}_1} \right\rangle \Bigg\}, \end{aligned} \tag{2.11}$$

where we have used the convention $(\mathbf{A}_1 \cdot \mathbf{B}_1)(\mathbf{A}_2 \cdot \mathbf{B}_2) = (\mathbf{A}_2\mathbf{A}_1) : (\mathbf{B}_1\mathbf{B}_2)$ and also its generalization to higher ordered products. The averages appearing in Eqs. (2.9)–(2.11) may, of course, be written as products of configuration and momentum averages. Since we have chosen to use a canonical distribution, we may easily compute the momentum averages which appear and thereby write the lower order coefficients as functions of configuration averages alone. The lower order coefficients in Eq. (2.8) may then be written as follows,

$$(0!)^{-1} \langle \mathbf{P}_1 \cdot (iL)^0 \mathbf{P}_1 \rangle = 3mkT, \tag{2.12}$$

$$(2!)^{-1} \langle \mathbf{P}_1 \cdot (iL)^2 \mathbf{P}_1 \rangle = -\frac{1}{2} kT \sum_{j=2}^{N} \left\langle \frac{d^2 u_{1j}}{dR_{1j}^2} + \frac{2}{R_{1j}} \frac{du_{1j}}{dR_{1j}} \right\rangle, \tag{2.13}$$

$$(4!)^{-1} \langle \mathbf{P}_1 \cdot (iL)^4 \mathbf{P}_1 \rangle = \frac{1}{24} \sum_{l=1}^{5} M_l \,, \tag{2.14}$$

where

$$M_1 = -\frac{1}{m}(kT)^2 \sum_{j=2}^{N} \left\langle 6\frac{d^4u_{1j}}{dR_{1j}^4} + \frac{8}{R_{1j}}\frac{d^3u_{1j}}{dR_{1j}^3} + \frac{16}{R_{1j}^2}\frac{d^2u_{1j}}{dR_{1j}^2} - \frac{24}{R_{1j}^3}\frac{du_{1j}}{dR_{1j}} \right\rangle, \tag{2.15}$$

$$M_2 = \frac{1}{m} kT \sum_{j=2}^{N} \left\langle \left(\frac{d^2u_{1j}}{dR_{1j}}\right)^2 + \frac{2}{R_{1j}^2}\left(\frac{du_{1j}}{dR_{1j}}\right)^2 + 3\frac{du_{1j}}{dR_{1j}}\frac{d^3u_{1j}}{dR_{1j}^3} \right\rangle, \tag{2.16}$$

$$M_3 = \frac{1}{m} kT \sum_{j=2}^{N} \sum_{\substack{k=2\\ \neq j}}^{N} \left\langle \frac{2}{R_{1j}}\frac{du_{1j}}{dR_{1j}}\frac{d^2u_{1k}}{dR_{1k}^2} + \frac{1}{R_{1j}R_{1k}}\frac{du_{1j}}{dR_{1j}}\frac{du_{1k}}{dR_{1k}} \right\rangle, \tag{2.17}$$

$$M_4 = \frac{3}{m} kT \sum_{j=2}^{N} \sum_{\substack{k=2\\ \neq j}}^{N} \left\langle \frac{\mathbf{R}_{1j}\cdot\mathbf{R}_{1k}}{R_{1j}R_{1k}}\frac{du_{1j}}{dR_{1j}}\frac{du_{1k}}{dR_{1k}} \right\rangle, \tag{2.18}$$

$$M_5 = \frac{1}{m} kT \sum_{j=2}^{N} \sum_{\substack{k=2\\ \neq j}}^{N} \left\langle \frac{\mathbf{R}_{1j}\mathbf{R}_{1j} : \mathbf{R}_{1k}\mathbf{R}_{1k}}{R_{1j}^2 R_{1k}^2} \left[\frac{d^2u_{1j}}{dR_{1j}^2}\frac{d^2u_{1k}}{dR_{1k}^2} \right.\right.$$

$$\left.\left. - \frac{2}{R_{1j}}\frac{du_{1j}}{dR_{1j}}\frac{d^2u_{1k}}{dR_{1k}^2} + \frac{1}{R_{1j}R_{1k}}\frac{du_{1j}}{dR_{1j}}\frac{du_{1k}}{dR_{1k}} \right] \right\rangle. \tag{2.19}$$

It should be mentioned that lengthy tensorial and algebraic manipulation is required to put the fourth-order coefficient in the form given by Eqs. (2.14)–(2.19). We have written the fourth-order coefficients in this form to expose certain differences in the nature of the terms involved. It may be noted that M_1 and M_2 involve averages over the positions of pairs of particles, while M_3, M_4, and M_5 involve averages over the positions of triplets. Further, M_1 differs from M_2 intrinsicly because, aside from temperature dependence arising in the configurational averages, it is explicitly proportional to the temperature squared whereas M_2 (also M_3, M_4, and M_5) is explicitly proportional only to the first power of the temperature. Also, M_3, M_4, and M_5 differ intrinsicly by virtue of of their varying dependence on the scaler products of the displacement vectors involved.

It is obvious that approximations must be introduced to carry out the computation of even the lower order coefficients in the expansion of $G_D(t)$. The higher order coefficients are even more complicated, so that we will not discuss their calculation, although, in principle, such calculation could be made.

Viscosity

For viscosity the dynamical variable of interest, $J_V(x, y)$ is the (x, y) component of the tensor J_v, defined by the relationship

$$\mathsf{J}_v = \frac{1}{m}\sum_{j=1}^{N} \mathbf{P}_j\mathbf{P}_j + \frac{1}{2}\sum_{j=1}^{N}\sum_{\substack{k=1\\ \neq j}}^{N} \mathbf{F}_{jk}\mathbf{R}_{jk}\,. \tag{2.20}$$

As for self-diffusion, the odd ordered coefficients in the expansion of the viscosity autocorrelation function

$$G_v = \sum_{n=0}^{\infty} (n!)^{-1} \langle J_v(x, y)(iL)^n J_v(x, y)\rangle\, t^n, \tag{2.21}$$

vanish, so that $G_v(t)$ is an even function. The first two nonzero coefficients in $G_v(t)$ may be written in the following forms:

$$(0!)^{-1} \langle J_v(x, y)(iL)^0 J_v(x, y)\rangle$$

$$= N(kT)^2 + \frac{1}{4}\sum_{i=1}^{N}\sum_{\substack{j=1\\ \neq i}}^{N}\sum_{k=1}^{N}\sum_{\substack{l=1\\ \neq k}}^{N} \left\langle \frac{R_{ij}(x)\, R_{ij}(y)\, R_{kl}(x)\, R_{kl}(y)}{R_{ij}R_{kl}} \frac{du_{ij}}{dR_{ij}} \frac{du_{kl}}{dR_{kl}} \right\rangle, \tag{2.22}$$

$$(2!)^{-1} \langle J_v(x, y)(iL)^2 J_v(x, y)\rangle$$

$$= \frac{1}{2}\sum_{i=1}^{N}\sum_{\substack{j=1\\ \neq i}}^{N}\sum_{k=1}^{N}\sum_{\substack{l=1\\ \neq k}}^{N} \left\langle \frac{R_{ij}(x)\, R_{ij}(y)\, R_{kl}(x)\, R_{kl}(y)}{R_{ij}^2 R_{kl}} \left(\frac{du_{ij}}{dR_{ij}}\right)^2 \frac{du_{kl}}{dR_{kl}} \right\rangle, \tag{2.23}$$

where $R_{ij}(x)$ and $R_{ij}(y)$ are the x and y components of the relative displacement vector $\mathbf{R}_{ij}$.

Thermal Conductivity

For thermal conductivity the dynamical quantity of interest $J_T(x)$ is the x component of the vector $\mathbf{J}_T$, defined by

$$\mathbf{J}_T = \frac{1}{m}\sum_{j=1}^{N}\left(\frac{\mathbf{P}_j \cdot \mathbf{P}_j}{2m}\right) - h\mathbf{P}_j + \frac{1}{2m}\sum_{j=1}^{N}\sum_{\substack{k=1\\ \neq j}}^{N}\left[u_{jk}\mathbf{P}_j - \frac{\mathbf{R}_{jk}}{R_{jk}}\frac{du_{jk}}{dR_{jk}}(\mathbf{R}_{jk}\cdot\mathbf{P}_j)\right], \tag{2.24}$$

where h is the enthalpy per particle. The odd ordered coefficients in the expansion of the thermal conductivity autocorrelation function

$$G_T(t) = \sum_{n=0}^{\infty} (n!)^{-1} \langle J_T(x)(iL)^n J_T(x)\rangle\, t^n \tag{2.25}$$

vanish, so that $G_T(t)$, like $G_D(t)$ and $G_v(t)$, is an even function. We will write out only the zeroth-order coefficient as it adequately demonstrates the type of calculation which may be expected in a thermal conductivity computation,

$$
\begin{aligned}
&(0!)^{-1} \langle J_T(x)(iL)^0 J_T(x)\rangle \\
&\quad = N\left[\frac{27}{4m}(kT)^3 - \frac{5h}{m}(kT)^2 + \frac{h^2}{m}kT\right] + \left[\frac{5}{2m}(kT)^2 - \frac{h}{m}kT\right]\sum_{j=1}^{N}\sum_{\substack{k=1\\ \neq j}}^{N} \\
&\quad\quad \times \left\langle u_{jk} - \frac{R_{jk}^2(x)}{R_{jk}}\frac{du_{jk}}{dR_{jk}}\right\rangle + \frac{1}{4m}kT\sum_{j=1}^{N}\sum_{\substack{k=1\\ \neq j}}^{N}\sum_{\substack{l=1\\ \neq j}}^{N} \\
&\quad\quad \times \left\langle u_{jk}u_{jl} - u_{jk}\frac{R_{jl}^2(x)}{R_{jl}}\frac{du_{jl}}{dR_{jl}} + (\mathbf{R}_{jk}\cdot\mathbf{R}_{jl})\frac{R_{jk}(x)\,R_{jl}(x)}{R_{jk}R_{jl}}\frac{du_{jk}}{dR_{jk}}\frac{du_{jl}}{dR_{jl}}\right\rangle. \quad (2.26)
\end{aligned}
$$

In summary, we see that the autocorrelation functions for self-diffusion, viscosity and thermal conductivity are all even functions of the time and that the lower order coefficients in their time series expansions are similar. We have discussed the viscosity and thermal conductivity autocorrelation functions to show the type of calculations involved in the computation of the lower order coefficients in $G_v(t)$ and $G_T(t)$. It is evident that the calculations implied by Eqs. (2.22) and (2.23) and Eq. (2.26) are similar in nature to those for M_5, the most complicated term in the fourth-order coefficient of $G_D(t)$. In fact, essentially similar methods may be used for the computation of the lower order coefficients in the expansion of each of the autocorrelation functions considered in this work. However, it does turn out that the first two nonzero coefficients in the expansion of $G_D(t)$ are easier to compute than any of the nonzero coefficients in the expansions of $G_v(t)$ and $G_T(t)$. This is the principal reason for our more detailed study of the self-diffusion autocorrelation function. However, approximate methods which may be used for the computation of the fourth- and higher-order coefficients in the expansion of $G_D(t)$ could be applied readily in the computation of the lower order coefficients in the expansions of $G_v(t)$ and $G_T(t)$.

3. APPROXIMATE SELF-DIFFUSION COEFFICIENT

Because the time series expansions given in Section 2 for the autocorrelation functions are general, one may choose arbitrarily the method for computation of the configurational averages in the expansion coefficients. But regardless of the method chosen, it is obvious that transport coefficients cannot be calculated merely by integrating separately each term in these expansions, since each resulting integral is divergent. However, as noted by Rice [7], the autocorrelation functions for dense fluids probably decay rapidly, so that approximate functions which are integrable and reproduce the exact autocorrelation functions for small times would presumably yield integrals which approximate the integrals of the exact autocorrelation functions. The series expansions of Section 2 are thus valuable to the extent that the lower order coefficients which may be calculated can be used to construct these approximate autocorrelation functions.

The simplest approximate self-diffusion autocorrelation function consistent with the assumption of rapid decay is the exponential form

$$G_D(t) = \frac{kT}{m} \exp(-\langle a \rangle\, t^2), \tag{3.1}$$

in which

$$a = \frac{1}{6m} \sum_{j=2}^{N} \left(\frac{d^2 u_{ij}}{dR_{ij}^2} + \frac{2}{R_{ij}} \frac{du_{ij}}{dR_{ij}} \right). \tag{3.2}$$

The approximate self-diffusion coefficient corresponding to this expression for $G_D(t)$ is

$$D = \frac{kT}{2m} \left(\frac{\pi}{\langle a \rangle} \right)^{1/2}. \tag{3.3}$$

The computational problem in this approximation is thus reduced to calculation of the configurational average $\langle a \rangle$. Douglass [6] has made this calculation using the radial distribution function approach; in this note we will consider only the cell model approach.

The cell method used here is a direct application of the method presented by Mayer and Careri [8] which allows for the cooperative motion of pairs of molecules and for all occupancy by a variable number of molecules. Mayer and Careri present pertinent relationships as well as numerical results for the calculation of thermodynamic functions in the special case of nearest neighbor interactions in a fcc lattice and cell occupancy by at most one molecule. The configurational probability distribution within each cell was assumed to be Gaussian. The pair potential which was used is a Morse-type potential with parameters determined by fitting the potential to the minimum in the Lennard–Jones (6–12) potential.

To avoid the duplicate presentation of many of the Mayer and Careri results, much of their notation will be employed here. The use of a Gaussian distribution yields for the joint distribution the relation

$$P(r_{ij}) = \left(\frac{\beta}{2^{2/3} \pi^{1/2}} \right)^3 \exp\left[- \left(\frac{\beta}{2^{2/3}} \right)^2 r_{ij}^2 \right]. \tag{3.4}$$

The quantity r_{ij} is the dimensionless distance between molecules i and j, $r_{ij} = R_{ij}/R$, where R is a scale parameter. The value of β is determined by minimization of the cell model expression for the configurational free energy. For sufficiently large values of β, roughly $\beta > 5$, $P(r_{ij}) \to 0$ at the cell boundary, so that integrations over cell volumes may be extended to $r_{ij} = \infty$ with little error. Use of Eq. (3.4) results in the following expression for $\langle a \rangle$:

$$\begin{aligned} \langle a \rangle &= \frac{12}{6m} \iiint P(r_{12}) \left[u''(Rr_{12}) + \frac{2}{Rr_{12}} u'(Rr_{12}) \right] d\mathbf{R}_{12} \\ &= \frac{24\pi}{6m} \int_0^\infty yP(y) \left\{ \int_{|2^{1/6}+y|}^{|2^{1/6}-y|} \left[u''(Rz) + \frac{2}{Rz} u'(Rz) \right] dz \right\} dy. \qquad (3.5) \end{aligned}$$

The Morse-type potential used by Mayer and Careri,

$$u(Rr) = u_0[\{\exp[-12(rx/2^{1/6} - 1)] - 2\exp[-6(rx/2^{1/6} - 1)]\}, \qquad (3.6)$$

where $x = 2^{1/6}R/R_e$, has a minimum of $-u_0$ at the equilibrium distance R_e, so that u_0 and R_e may be taken to be the corresponding Lennard–Jones (6–12) parameters. With omission of terms which are negligible if β is sufficiently large, the integrations in Eq. (3.5) yield

$$\begin{aligned} \langle a \rangle = 298 \left(\frac{u_0}{mR_e^2} \right) \{ &2(1 - 12x/\beta^2) \exp[72(x/\beta)^2 - 12x + 12] \\ &- (1 - 6x/\beta^2) \exp[18(x/\beta)^2 - 6x + 6] \}. \qquad (3.7) \end{aligned}$$

To obtain numerical values for $\langle a \rangle$, x and β must be determined. The quantity x is directly related to ρ, the ratio of the number of molecules in the system to the number of cells, which like β is determined by minimization of the configuration free energy. The relation between x and ρ is $\rho = x^3 v_0/v$, where v is the volume per molecule and v_0 is the volume per molecule at absolute zero temperature, $v_0 = 2^{-1/2}R_e^3$. Reference [8] should be consulted for the details of calculation of β and ρ.

To provide a comparison of calculated and experimental self-diffusion coefficients, the approximate self-diffusion coefficient given by Eq. (3.3) was calculated for liquid argon at 84°K. The values of the Lennard–Jones (6–12) potential parameters [9] used in this calculation are $u_0/k = 116$°K, $R_e = 3.889 \times 10^{-8}$ cm. The density [10] was taken to be 1.423 g/cc. Using these values, the calculated self-diffusion coefficient is 2.28×10^{-5} cm^2/sec, which compares favorably with the experimental value of $(2.07 \pm 0.06) \times 10^{-5}$ cm^2/sec reported by Corbett and Wang [11]. Although, as stated previously, little theoretical significance may be placed on this result, it is interesting to note that the calculated value resulting from the exponential approximation in Eq. (3.1) is larger than the experimental value. This would be expected if approximate functions were indeed capable of describing the behavior of the exact correlation function. This follows since, as pointed out by Rice [7], the self-diffusion autocorrelation function would be expected to oscillate about zero before asymptotically vanishing, whereas the exponential approximation does not allow oscillations. Of course, approximate correlation functions which do oscillate about zero may be constructed if higher order coefficients in the series expansions are computed.

Two other results of the calculation of this section should be mentioned, namely the values of β and ρ determined by minimization of the configurational free energy, these are $\beta = 9.8$ and $\rho = 0.999$. The fact that $\beta > 5$ justifies the integration over all space rather than only over the cell volume. The fact that ρ is near unity justifies to some extent the use of a cell model, for if ρ were appreciably less than unity the number of nearest neighbors would be diminished accordingly. If there were fewer nearest neighbors, the decay of the self-diffusion autocorrelation function would presumably be less rapid and the exponential approximation less accurate.

4. Higher Order Approximations

The principal deterrent to calculations of higher order approximations to the autocorrelation functions is the fact that averages over the positions of more than two molecules must be computed. Because there are presently no methods which allow for the cooperative motion of more than two molecules in a rigorous manner, approximations even more drastic than those already introduced in Section 3 must be employed.

We have developed one possible approach and have carried out computations through the fourth-order coefficient in the expansion of the self-diffusion autocorrelation function. This allows the use of such approximate functions as the exponentially damped cosine function

$$G_D(t) = \exp(-\langle a\rangle t^2) \cos[(\langle a\rangle^2 - s\langle b\rangle)^{1/2} t^4], \tag{4.1}$$

where a is again the quantity given by Eq. (3.2) while b is given by the relation

$$b = (72\, mkT)^{-1} \sum_{l=1}^{5} M_l\, ,$$

with $M_1 - M_5$ defined by Eqs. (2.15)–(2.19). It is for the computation of $\langle b\rangle$ that a cell method permitting the calculation of configurational averages involving more than two molecules is required. To complicate matters, averages of tensor quantities of as high as second order must be computed. These calculations are considerably more involved than calculations of scaler averages. In addition, scaler products of these tensor averages must be computed for the particular lattice configuration chosen. Therefore, because of the lengthy nature of the development of the cell method and the final expression for $\langle b \rangle$, and because the calculations which have been made must be considered tentative, no details will be presented at this time. We will merely relate the tentative result, $D_{\text{calc}} = 1.96 \times 10^{-5}\,\text{cm}^2/\text{sec}$, obtained by use of the approximate self-diffusion autocorrelation given in Eq. (4.1).

5. Discussion

The purpose of this presentation has been to demonstrate the feasibility of using the cell method in the framework of the time-correlation function theory of transport properties. We have chosen to carry out explicit calculations for the self-diffusion autocorrelation function as a demonstration of the type of computation required for the calculation of this and other transport coefficient autocorrelation functions. Using a simple approximation to the autocorrelation function we have computed a corresponding approximate self-diffusion coefficient for liquid argon which is only about 10% greater than the reported experimental value. Some of the problems encountered in the computation of higher order approximations have been discussed.

Due to the numerous approximations employed, no special significance may be placed on the fact that the calculated self-diffusion coefficient agrees so favorably with the experimental value. However, it does give some evidence to the feasibility of using the cell model approach for the calculation of approximate transport coefficients. It is anticipated that such calculations will generally be most accurate when applied to very high density fluids. Continued study of approaches to the calculation of higher order coefficients in the expansions of the autocorrelation functions would undoubtedly be of value.

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