

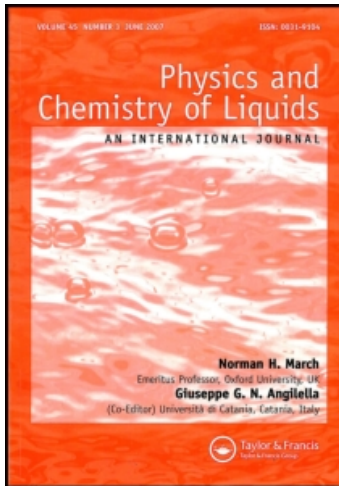
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T. Gaskell^a

^a Department of Physics, The University Sheffield,

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A Theory of the Diffusion Coefficient in a Liquid Metal: I

T. GASKELL

Department of Physics
The University
Sheffield

Abstract—An expression has been derived for the diffusion coefficient in terms of the interatomic potential, the pair distribution function and the self-correlation function in a liquid. By making use of an earlier result for the time-dependent pair distribution function, which includes correlation in the relative motion of two atoms, the expression has been made applicable to any type of interatomic core potential. In particular it will be useful in a liquid metal where a relatively soft core is a generally accepted feature of the effective interionic potential.

1. Introduction

In a recent paper⁽¹⁾ a first principles calculation of the velocity autocorrelation function and diffusion coefficient in a dense classical liquid has been attempted. It was necessary in this calculation to separate the core from the relatively weak longer ranged part of the potential and to treat its effect separately in a physically realistic way. The method involved was we believe probably most satisfactory for a perfectly rigid core, although it has been applied with success to liquid argon in conditions closely corresponding to the triple point. In this case a 6-12 potential was assumed to be adequate to describe the interatomic forces, with an appropriate definition of the core, as discussed by Barker and Gaskell.⁽²⁾

In a liquid metal the softer core,⁽³⁾ which is generally thought to be more appropriate to an effective interionic potential in these liquids, makes the applications of the above theory somewhat less satisfactory bearing in mind that the approximations involved in the calculation of the velocity autocorrelation function were designed for a rigid core. This work has been carried out to try to overcome the problem of having to separate the potential in this way, and to derive an expression for the diffusion coefficient in a liquid metal in

which both parts of the potential i.e. the relatively soft core and long range oscillatory tail were automatically taken into account.

The velocity autocorrelation function is defined as $\langle \mathbf{v}_i(t) \cdot \mathbf{v}_i(0) \rangle$ where $\mathbf{v}_i(t)$ denotes the velocity of any atom in the liquid at time t and the brackets a canonical ensemble average. If we describe the normalized velocity autocorrelation function $\langle \mathbf{v}_i(t) \cdot \mathbf{v}_i(0) \rangle / \langle \mathbf{v}_i^2(0) \rangle$ by $\psi(t)$ the basis of our approach is to derive an equation of the form

$$\frac{d}{dt} \psi(t) + \int_0^t d\tau K(\tau) \psi(t - \tau) = 0 \quad (1.1)$$

where the kernel of this integrodifferential equation $K(\tau)$ has the intuitive interpretation of a "memory" function.⁽⁴⁾ It is well known that the diffusion coefficient, D , is given by the equation

$$D = \frac{k_B T}{m} \int_0^\infty dt \psi(t),$$

m being the atomic mass.

2. Derivation of the Memory Function

Consider the equation of motion of one of the atoms in the liquid whose position and velocity we describe by $\mathbf{x}_i(t)$ and $\mathbf{v}_i(t)$ respectively. It is given by

$$m \frac{d}{dt} \mathbf{v}_i(t) = - \sum_{j \neq i} \nabla_i \phi(|\mathbf{x}_i(t) - \mathbf{x}_j(t)|) \quad (2.1)$$

where the summation extends over the other atoms in the liquid. We shall obtain from this equation a result for the velocity autocorrelation function of the form of (1.1). Although an exact expression for the memory function was given by Zwanzig⁽⁵⁾ in terms of a projection operator, only limited success has been achieved in attempts to evaluate the expression in a practical application,⁽⁶⁾ especially in the problem of taking into account the effects of a strongly repulsive atomic core. Instead of using the formally exact expression for the memory function we prefer instead to start from Eq. (2.1) and use a rather more intuitive approach.

We form the scalar product of both sides of Eq. (2.1) with $\mathbf{v}_i(s)$ for some time $s < t$, to give

$$\begin{aligned} m \frac{d\mathbf{v}_i}{dt}(t) \cdot \mathbf{v}_i(s) &= - \sum_{j \neq i} \mathbf{v}_i(s) \cdot \nabla_i \phi(|\mathbf{x}_i(t) - \mathbf{x}_j(t)|) \\ &= - \sum_{j \neq i} \{\mathbf{v}_i(s) - \mathbf{v}_j(s)\} \cdot \nabla_i \phi(|\mathbf{x}_i(t) - \mathbf{x}_j(t)|) \\ &\quad - \sum_{j \neq i} \mathbf{v}_j(s) \cdot \nabla_i \phi(|\mathbf{x}_i(t) - \mathbf{x}_j(t)|) \\ &= - \sum_{j \neq i} \mathbf{v}_{ij}(s) \cdot \nabla_i \phi(|\mathbf{x}_i(t) - \mathbf{x}_j(t)|) \\ &\quad + \sum_{j \neq i} \mathbf{v}_j(s) \cdot \nabla_j \phi(|\mathbf{x}_j(t) - \mathbf{x}_i(t)|) \end{aligned}$$

By summing over the labels i on both sides of this equation⁽²⁾ we obtain

$$\begin{aligned} m \sum_i \frac{d\mathbf{v}_i}{dt}(t) \cdot \mathbf{v}_i(s) &= - \sum_i \sum_{j \neq i} \mathbf{v}_{ij}(s) \cdot \nabla_i \phi(|\mathbf{x}_i(t) - \mathbf{x}_j(t)|) \\ &\quad + \sum_j \sum_{i \neq j} \mathbf{v}_j(s) \cdot \nabla_j \phi(|\mathbf{x}_j(t) - \mathbf{x}_i(t)|) \end{aligned}$$

The second term on the right hand side of this equation may be written

$$- m \sum_j \frac{d\mathbf{v}_j}{dt}(t) \cdot \mathbf{v}_j(s)$$

and therefore the equation becomes

$$2m \sum_i \frac{d\mathbf{v}_i}{dt}(t) \cdot \mathbf{v}_i(s) = - \sum_i \sum_{j \neq i} \mathbf{v}_{ij}(s) \cdot \nabla_i \phi(|\mathbf{x}_i(t) - \mathbf{x}_j(t)|)$$

Each term in the summation over the label i is identical when we take a canonical ensemble average of both sides and therefore we may write

$$m \left\langle \frac{d\mathbf{v}_i}{dt}(t) \cdot \mathbf{v}_i(s) \right\rangle = - \frac{1}{2} \left\langle \sum_{j \neq i} \mathbf{v}_{ij}(s) \cdot \nabla_i \phi(|\mathbf{x}_i(t) - \mathbf{x}_j(t)|) \right\rangle$$

and because the potential depends on x_{ij} we may replace ∇_i by ∇_{ij} and finally obtain the result which forms the basis of our calculation,

namely

$$\begin{aligned}
 & m \left\langle \frac{d\mathbf{v}_i}{dt}(t) \cdot \mathbf{v}_i(s) \right\rangle \\
 &= -\frac{1}{2} \left\langle \sum_{j \neq i} \mathbf{v}_{ij}(s) \cdot \nabla_{ij} \phi(|\mathbf{x}_i(t) - \mathbf{x}_j(t)|) \right\rangle \\
 &= -\frac{1}{2} \left\langle \sum_{j \neq i} \int d\mathbf{x} \mathbf{v}_{ij}(s) \cdot \nabla \phi(x) \delta(\mathbf{x} - \mathbf{x}_{ij}(t)) \right\rangle \\
 &= -\frac{1}{16\pi^3} \left\langle \sum_{j \neq i} \int d\mathbf{q} \int d\mathbf{x} \mathbf{v}_{ij}(s) \cdot \nabla \phi(x) \exp[i\mathbf{q} \cdot (\mathbf{x} - \mathbf{x}_{ij}(t))] \right\rangle \quad (2.2)
 \end{aligned}$$

Carrying out the angular integration with respect to \mathbf{x} this latter expression may be written as

$$\begin{aligned}
 & m \left\langle \frac{d\mathbf{v}_i}{dt}(t) \cdot \mathbf{v}_i(s) \right\rangle \\
 &= -\frac{1}{4\pi^2} \sum_{j \neq i} \int d\mathbf{q} \int_0^\infty dx x^3 f(qx) \frac{d\phi}{dx} \langle i\mathbf{q} \cdot \mathbf{v}_{ij}(s) \exp(-i\mathbf{q} \cdot \mathbf{x}_{ij}(t)) \rangle \quad (2.3)
 \end{aligned}$$

where $f(qx) = (\sin(qx) - qx \cos(qx))/(qx)^3$. Using the identity

$$x^3 f(qx) = -\frac{x^2}{q^2} \frac{d}{dx} \frac{\sin(qx)}{qx}$$

Eq. (2.3) can be put in the alternative form

$$\begin{aligned}
 & m \left\langle \frac{d\mathbf{v}_i}{dt}(t) \cdot \mathbf{v}_i(s) \right\rangle \\
 &= \frac{1}{4\pi^2} \sum_{j \neq i} \int_0^\infty dx x^2 \frac{d\phi}{dx} \frac{d}{dx} \int d\mathbf{q} \frac{1}{q^2} \frac{\sin(qx)}{qx} \langle i\mathbf{q} \cdot \mathbf{v}_{ij}(s) \exp(-i\mathbf{q} \cdot \mathbf{x}_{ij}(t)) \rangle
 \end{aligned}$$

If we replace at this stage the angular integration with respect to \mathbf{x} the above expression may be written

$$\begin{aligned}
 & m \left\langle \frac{d\mathbf{v}_i}{dt}(t) \cdot \mathbf{v}_i(s) \right\rangle \\
 &= \frac{1}{16\pi^3} \sum_{j \neq i} \int d\mathbf{x} \frac{d\phi}{dx} \frac{d}{dx} \int d\mathbf{q} \frac{1}{q^2} \langle i\mathbf{q} \cdot \mathbf{v}_{ij}(s) \exp[-i\mathbf{q} \cdot (\mathbf{x}_{ij}(t) - \mathbf{x})] \rangle \quad (2.4)
 \end{aligned}$$

Remembering that the left hand side of this equation is the time derivative of a function of the time difference $t - s$, it is easily seen that interchanging the time variables on the right hand side of the

average only changes the sign of the equation and therefore we may write

$$\begin{aligned}
 m \left\langle \frac{d\mathbf{v}_i}{dt}(t) \cdot \mathbf{v}_i(s) \right\rangle &= -\frac{1}{16\pi^3} \sum_{j \neq i} \int d\mathbf{x} \frac{d\phi}{dx} \frac{d}{dx} \int d\mathbf{q} \frac{1}{q^2} \langle i\mathbf{q} \cdot \mathbf{v}_{ij}(t) \exp[-i\mathbf{q} \cdot (\mathbf{x}_{ij}(s) - \mathbf{x})] \rangle \\
 &\hspace{20em} (2.5)
 \end{aligned}$$

Bearing in mind that we are looking for a result in the form (1.1) we shall rewrite the latter equation by making use of the following identity

$$\begin{aligned}
 \langle -i\mathbf{q} \cdot \mathbf{v}_{ij}(t) \exp[-i\mathbf{q} \cdot (\mathbf{x}_{ij}(s) - \mathbf{x})] \rangle &= \int_s^t d\tau \frac{d}{d\tau} \langle i\mathbf{q} \cdot \mathbf{v}_{ij}(t) \exp[-i\mathbf{q} \cdot (\mathbf{x}_{ij}(\tau) - \mathbf{x})] \rangle \\
 &= \int_s^t d\tau \langle (\mathbf{q} \cdot \mathbf{v}_{ij}(t))(\mathbf{q} \cdot \mathbf{v}_{ij}(\tau)) \exp[-i\mathbf{q} \cdot (\mathbf{x}_{ij}(\tau) - \mathbf{x})] \rangle
 \end{aligned}$$

and hence

$$\begin{aligned}
 m \left\langle \frac{d\mathbf{v}_i}{dt}(t) \cdot \mathbf{v}_i(s) \right\rangle &= \frac{1}{16\pi^3} \int_s^t d\tau \sum_{j \neq i} \int d\mathbf{x} \frac{d\phi}{dx} \frac{d}{dx} \\
 &\cdot \int d\mathbf{q} \frac{1}{q^2} \langle (\mathbf{q} \cdot \mathbf{v}_{ij}(t))(\mathbf{q} \cdot \mathbf{v}_{ij}(\tau)) \exp[-i\mathbf{q} \cdot (\mathbf{x}_{ij}(\tau) - \mathbf{x})] \rangle \quad (2.6)
 \end{aligned}$$

Thus far the equation is exact but in order to proceed further we shall at this stage have to evaluate the ensemble average in an approximate way, beginning with the extraction of the initial configurations of the atoms from the exponent.

Hence we write (2.6) in the following way

$$\begin{aligned}
 m \left\langle \frac{d\mathbf{v}_i}{dt}(t) \cdot \mathbf{v}_i(s) \right\rangle &= \frac{1}{16\pi^3} \int_s^t d\tau \sum_{j \neq i} \int d\mathbf{x} \frac{d\phi}{dx} \frac{d}{dx} \int d\mathbf{y} \\
 &\cdot \int d\mathbf{q} \frac{1}{q^2} \langle (\mathbf{q} \cdot \mathbf{v}_{ij}(t))(\mathbf{q} \cdot \mathbf{v}_{ij}(\tau)) \\
 &\cdot \exp[-i\mathbf{q} \cdot (\mathbf{x}_{ij}(\tau) - \mathbf{x}_{ij}(s) - \mathbf{y})] \delta(\mathbf{x} - \mathbf{y} - \mathbf{x}_{ij}(s)) \rangle \\
 &\hspace{20em} (2.7)
 \end{aligned}$$

Now the expression within the averaging brackets can virtually be broken down into three periods of time, (i) the delta function which involves the initial configurations of the atoms, (ii) the period in

which the atoms interact, i.e. from $s \rightarrow \tau$, occurring in the variables within the exponent and finally (iii) the velocities being explicit functions of time from $\tau \rightarrow t$. We shall use an approximate procedure, somewhat similar to the spirit of the well known Vineyard approximation (although that was originally applied to a different problem), of averaging over the initial configurations of the atoms, then allowing them to migrate to their final positions $\mathbf{x}_{ij}(\tau)$, and finally, consistent with this first step, an average over the final velocities of the atoms. Therefore (2.7) becomes

$$\begin{aligned}
 m \left\langle \frac{d\mathbf{v}_i}{dt}(t) \cdot \mathbf{v}_i(s) \right\rangle & \simeq \frac{1}{16\pi^3} \int_s^t d\tau \sum_{j \neq i} \int d\mathbf{x} \frac{d\phi}{d\mathbf{x}} \frac{d}{d\mathbf{x}} \int d\mathbf{y} \int d\mathbf{q} \frac{1}{q^2} \langle (\mathbf{q} \cdot \mathbf{v}_{ij}(t)) (\mathbf{q} \cdot \mathbf{v}_{ij}(\tau)) \rangle \\
 & \cdot \langle \exp[-i\mathbf{q} \cdot (\mathbf{x}_{ij}(\tau) - \mathbf{x}_{ij}(s) - \mathbf{y})] \rangle \langle \delta(\mathbf{x} - \mathbf{y} - \mathbf{x}_{ij}(s)) \rangle \quad (2.8)
 \end{aligned}$$

Now since

$$\langle (\mathbf{q} \cdot \mathbf{v}_{ij}(t)) (\mathbf{q} \cdot \mathbf{v}_{ij}(\tau)) \rangle = \frac{q^2}{3} \langle \mathbf{v}_{ij}(t) \cdot \mathbf{v}_{ij}(\tau) \rangle$$

and

$$\langle \delta(\mathbf{x} - \mathbf{y} - \mathbf{x}_{ij}(s)) \rangle = \frac{1}{V} g(|\mathbf{x} - \mathbf{y}|)$$

where $g(|\mathbf{x} - \mathbf{y}|)$ is the radial distribution function for the liquid we are able to express (2.8) as

$$\begin{aligned}
 m \left\langle \frac{d\mathbf{v}_i}{dt}(t) \cdot \mathbf{v}_i(s) \right\rangle & = \frac{\rho}{6} \int_s^t d\tau \langle \mathbf{v}_{ij}(t) \cdot \mathbf{v}_{ij}(\tau) \rangle \int d\mathbf{x} \frac{d\phi}{d\mathbf{x}} \int d\mathbf{y} \\
 & \cdot \langle \delta(\mathbf{y} - \mathbf{x}_{ij}(\tau) + \mathbf{x}_{ij}(s)) \rangle \frac{d}{d\mathbf{x}} g(|\mathbf{x} - \mathbf{y}|) \\
 & = \frac{\rho}{6} \int_s^t d\tau \langle \mathbf{v}_{ij}(t) \cdot \mathbf{v}_{ij}(\tau) \rangle \int d\mathbf{x} \frac{d\phi}{d\mathbf{x}} \int d\mathbf{y} \\
 & \cdot G_R(\mathbf{y}, \tau - s) \frac{d}{d\mathbf{x}} g(|\mathbf{x} - \mathbf{y}|) \quad (2.9)
 \end{aligned}$$

ρ as usual denoting the atomic density and

$$G_R(\mathbf{y}, \tau - s) \equiv \langle \delta(\mathbf{y} - \mathbf{x}_{ij}(\tau) + \mathbf{x}_{ij}(s)) \rangle$$

is a function which describes the relative motion of two atoms in the liquid (the labels i, j now refer to any two atoms in the

ensemble), being essentially the probability that the change in interatomic separation between two atoms i and j in time $\tau - s$ is y . It has been pointed out⁽¹⁾ that if it is assumed in performing this average that each atom migrates independently from its initial to its final position $G_R(y, \tau - s)$ has the same form, within the Gaussian approximation, of the self-correlation function but with the introduction of an effective mass m^* . Hence approximately

$$G_R(y, \tau - s) = \{4\pi a(\tau - s)\}^{-3/2} \exp(-y^2/4a(\tau - s)) \equiv G_s^*(y, \tau - s) \quad (2.10)$$

with

$$a(t) = \frac{k_B T'}{m^*} \int_0^t d\tau (t - \tau) \psi(\tau)$$

and $m^* = m/2$, the reduced mass in the relative motion of the two atoms. Along with this approach we shall write

$$\langle \mathbf{v}_{ij}(t) \cdot \mathbf{v}_{ij}(\tau) \rangle = \langle (\mathbf{v}_i(t) - \mathbf{v}_j(t)) \cdot (\mathbf{v}_i(\tau) - \mathbf{v}_j(\tau)) \rangle = 2 \langle \mathbf{v}_i(t) \cdot \mathbf{v}_i(\tau) \rangle$$

having neglected correlations of the type $\langle \mathbf{v}_i(t) \cdot \mathbf{v}_j(\tau) \rangle$. It is true that when $t = \tau$ the velocities of the two atoms are statistically independent and $\langle \mathbf{v}_i(t) \cdot \mathbf{v}_j(t) \rangle = 0$, but the omission of this term when $t \neq \tau$ is consistent with the assumption above that the two atoms move independently.

Therefore (2.9), within this scheme, can clearly be written in the required form (now putting $s = 0$)

$$\frac{d}{dt} \psi(t) + \int_0^t d\tau K(\tau) \psi(t - \tau) = 0$$

with

$$K(\tau) = -\frac{\rho}{3m} \int d\mathbf{x} \frac{d\phi}{dx}(x) \int d\mathbf{y} G_s^*(y, \tau) \frac{d}{dx} g(|\mathbf{x} - \mathbf{y}|) \quad (2.11)$$

which was the stated purpose of this section.

Two comments can be made immediately about the memory function, $K(\tau)$, defined above. The first is that its value at $\tau = 0$

$$K(0) = -\frac{\rho}{3m} \int d\mathbf{x} \frac{d\phi}{dx}(x) \frac{dg}{dx}(x) = \frac{\rho}{3m} \int d\mathbf{x} g(x) \nabla^2 \phi(x)$$

is exact. It is easily demonstrated that this guarantees the correct behaviour of the calculated correlation function $\psi(t)$, at sufficiently

small t , because the coefficient of t^2 in the expansion

$$\psi(t) = 1 + \ddot{\psi}(0) \frac{t^2}{2} + \dots$$

will be exact, being given by $\ddot{\psi}(0) = -K(0)$. The second is that the decoupling procedure we have adopted allows the particles to approach each other arbitrarily closely for $\tau > 0$ and the integrations in the definition of the memory function will be divergent for a sufficiently hard core. $K(\tau)$ therefore will not exist for this type of potential. The problem we shall try to solve in the next section is that of modifying the above memory function in such a way that it will be defined for a potential which is singular at the origin, and at the same time maintaining the known exact value of the memory function at $\tau = 0$.

3. Modified Memory Function: Correlated Motion of the Atoms

The difficulty of using the latter formulation of the memory function with a singular potential arises when we average at an earlier stage over the initial configurations of the atoms and then allow them to migrate to their final positions. To overcome the problem we must build in some correlation also in their final positions and this we achieve in the following way.

Some years ago Oppenheim and Bloom⁽⁷⁾ discussed the evaluation of a correlation function involving the relative motion of two atoms in a liquid, being essentially the probability that at $t = 0$ two atoms will be a distance \mathbf{r} apart while at $t = \tau$ the separation of the same two atoms will be \mathbf{x} , i.e. the ensemble average (N being the number of atoms)

$$\frac{1}{N} \sum_{i,j(i \neq j)} \langle \delta(\mathbf{r} - \mathbf{x}_{ij}(0)) \delta(\mathbf{x} - \mathbf{x}_{ij}(\tau)) \rangle \equiv G_R(\mathbf{r}, \mathbf{x}, \tau) \quad (3.1)$$

If we use the approximation of extracting the time dependent part by writing this as $\langle \delta(\mathbf{x} - \mathbf{r} - \mathbf{x}_{ij}(\tau) + \mathbf{x}_{ij}(0)) \delta(\mathbf{r} - \mathbf{x}_{ij}(0)) \rangle$ and then averaging over the initial configurations of the atoms, as we did in the previous section to derive the memory function, we obtain

$$\begin{aligned} G(\mathbf{r}, \mathbf{x}, \tau) &\simeq \frac{1}{N} \sum_{i,j(i \neq j)} \langle \delta(\mathbf{r} - \mathbf{x}_{ij}(0)) \rangle \langle \delta(\mathbf{x} - \mathbf{r} - \mathbf{x}_{ij}(\tau) + \mathbf{x}_{ij}(0)) \rangle \\ &\simeq \rho g(\tau) \langle \delta(\mathbf{x} - \mathbf{r} - \mathbf{x}_{ij}(\tau) + \mathbf{x}_{ij}(0)) \rangle, \end{aligned} \quad (3.2)$$

(i, j again refer to any two atoms in the ensemble). We could now use Eq. (2.10) to evaluate the time dependent part of the above expression. A more satisfactory approximation, in which the atoms are correlated in both their initial and final positions (as they should be), was derived by Oppenheim and Bloom, and is given by

$$G(\mathbf{r}, \mathbf{x}, \tau) \simeq \rho g^{1/2}(r) g^{1/2}(x) \{8\pi D\tau\}^{-3/2} \exp(-|\mathbf{x} - \mathbf{r}|^2/8D\tau) \quad (3.3)$$

The accuracy of this result is extremely difficult to assess, since it is based on a number of approximations (notably a constant acceleration approximation), but it is interesting to note that the time dependent part of this expression has the form of the hydrodynamic limit of the self-correlation function in a fluid but with an effective mass $m^* = m/2$. Indeed $G_s^*(y, \tau)$ defined in (2.10) has exactly this form as sufficiently large τ . We therefore make the further assumption that a suitable extrapolation of Eq. (3.3), to achieve a result to cover all values of τ , is to replace the time dependent part of (3.3) by $G_s^*(|\mathbf{x} - \mathbf{r}|, \tau)$ as defined in (2.10). Therefore we finally obtain for the so-called time dependent pair distribution function

$$G(\mathbf{r}, \mathbf{x}, \tau) \simeq \rho g^{1/2}(r) g^{1/2}(x) G_s^*(|\mathbf{x} - \mathbf{r}|, \tau) \quad (3.4)$$

Comparing (3.2) and (3.4) suggests that to recover the result (3.4), after making the approximation of decoupling and averaging over the initial atomic configurations, we must make the replacement

$$\langle \delta(\mathbf{x} - \mathbf{r} - \mathbf{x}_{ij}(\tau) + \mathbf{x}_{ij}(0)) \rangle \simeq \frac{g^{1/2}(x)}{g^{1/2}(r)} G_s^*(|\mathbf{x} - \mathbf{r}|, \tau) \quad (3.5)$$

in order that the relative motion of the atoms be correlated at all times. Because we have used precisely the same initial decoupling scheme to give the result (2.9), we argue that its most serious defect, namely the subsequent uncorrelated motion of the atoms, can be corrected by making the modification shown in the latter equation. By decoupling in the way we have indicated, we have clearly lost the constraint imposed by knowing that the final separation of the atoms is \mathbf{x} . The latter step reimposes this condition. With this correction therefore the memory function becomes

$$K(\tau) = -\frac{\rho}{3m} \int d\mathbf{x} \frac{d\phi}{dx} \int d\mathbf{y} \frac{g^{1/2}(x)}{g^{1/2}(|\mathbf{x} - \mathbf{y}|)} G_s^*(y, \tau) \frac{d}{dx} g(|\mathbf{x} - \mathbf{y}|) \quad (3.6)$$

It is once again easily confirmed that $K(0)$ is exact.

Remembering that the pair distribution function may be written $g(r) = \exp[-u(r)/k_B T]$, where $u(r)$ is the potential of mean force, it quickly follows

$$\frac{1}{g^{1/2}(|\mathbf{x} - \mathbf{y}|)} \frac{d}{d\mathbf{x}} g(|\mathbf{x} - \mathbf{y}|) = 2 \frac{d}{d\mathbf{x}} g^{1/2}(|\mathbf{x} - \mathbf{y}|)$$

and the memory function may be more conveniently expressed as

$$K(\tau) = -\frac{2\rho}{3m} \int d\mathbf{x} g^{1/2}(x) \frac{d\phi}{d\mathbf{x}} \frac{d}{d\mathbf{x}} \int d\mathbf{y} G_s^*(\mathbf{y}, \tau) g^{1/2}(|\mathbf{x} - \mathbf{y}|)$$

or alternatively (3.7)

$$= \frac{2\rho}{3m} \int d\mathbf{x} \left[g^{1/2}(x) \nabla^2 \phi(x) + \frac{d\phi}{d\mathbf{x}}(x) \frac{dg^{1/2}}{d\mathbf{x}}(x) \right] \cdot \int d\mathbf{y} G_s^*(\mathbf{y}, \tau) g^{1/2}(|\mathbf{x} - \mathbf{y}|)$$

the last step following on integrating by parts. From a computational point of view the first of the latter equations is probably the most useful, because in a practical application of these results to a liquid metal it will be necessary to use tabulated values of the radial distribution function obtained from molecular dynamics calculations,⁽⁸⁾ and this expression can be conveniently written in terms of $g^{1/2}(x)$ only, without involving its derivative.

It is well known that (1.1) can be quickly solved by means of the Laplace transform subject to the boundary condition $\psi(0) = 1$, and that the diffusion coefficient is given in terms of the memory function by

$$D = \frac{k_B T}{m} \left\{ \int_0^\infty dt K(t) \right\}^{-1}.$$

4. Discussion

In a number of recent attempts to produce a first principles calculation of the velocity autocorrelation function in a dense fluid, the problem of successfully handling the strongly repulsive core of the interatomic force has turned out to be one of the most troublesome,^(1,6,9) although progress has been made in the case of a perfectly rigid core.⁽¹⁾ The decoupling scheme we have used in order to derive an expression for the memory function is basically similar to that

employed with some success in an earlier calculation in liquid argon,⁽²⁾ but the approach has been modified in an attempt to solve the difficult problem of describing the correlated relative motion of two atoms over a period of time. The inclusion of correlation in the atomic dynamics has been achieved by making use of an earlier result for the time-dependent pair distribution function derived by Oppenheim and Bloom. As always in a complex many-body problem, approximations are difficult to justify and we must at least try to ensure in our decoupling scheme that the known behaviour of the velocity autocorrelation function in some limit is correctly reproduced, in this case the time expansion in the limit $t \rightarrow 0$. Incidentally the Eqs. (3.7) are not defined for a rigid core interaction, because of the discontinuous nature of the function $g^{1/2}(x)$ in this case.

We eventually derive an expression for the memory function, $K(t)$, which is defined for a continuous though strongly repulsive potential for all values of t . It remains to examine the validity of the approach by means of a practical application of the result, if sufficiently detailed information about the pair distribution function in a liquid metal becomes available, preferably over a range of densities.

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