

Theory of self-diffusion in liquids

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A new theory of self-diffusion in simple liquids is outlined. Dynamical superposition is assumed and then it is shown that with no further approximations the self-diffusion coefficient can be computed if the functional form of the equilibrium pair correlation function $g(r)$ is known. The result is formally equivalent to that found in the theory of dilute gases with the potential of mean force, $w(r) = -\ln g(r)$, taking the place of the intermolecular potential.

There have been various attempts to use the Bogoliubov-Born-Green-Kirkwood-Yvon (BBGKY) hierarchy as the basis for a theory of transport applicable to simple liquids and dense fluids¹⁻³; none has been conspicuously successful. We outline a treatment of self-diffusion based upon the dynamical superposition approximation (DSA), which explicitly neglects nonequilibrium three-particle correlations.⁴ Within this framework an exact solution, valid in the hydrodynamic domain, is found.

In a two-component system slightly displaced from equilibrium containing equal concentrations of mechanically identical distinguishable molecules, the one- and two-particle reduced distribution functions (RDF) are

$$\begin{aligned} F_a(1) &= \varphi(1) [1 + \sigma_a(1)], \\ F_{ab}(12) &= \varphi(1)\varphi(2)g(r) [1 + \sigma_a(1) + \sigma_b(2) + \sigma_{ab}(12)], \end{aligned} \quad (1)$$

where $\varphi(i)$ is the Boltzmann factor, $g(r)$ is the radial distribution function, the quantities $\sigma_a(1)$ and $\sigma_{ab}(12)$ refer to the nonequilibrium parts of the singlet and doublet RDF's which satisfy the sum rules $\sum_a \sigma_a(1) = 0$ and $\sum_a \sum_b \sigma_{ab}(12) = 0$, and where $\sigma_{ab}(12) \rightarrow 0$ as $r_{12} \rightarrow \infty$. From hydrodynamics we know that a single Fourier component of a concentration displacement decays as $f(t) = e^{-k^2 D t}$. We may create the statistical-mechanical analog of such a concentration wave by imposing a periodic external field.⁵ At $t=0$ the field is turned off; after an induction period $t_0(k)$, during which the system settles into its long-time behavior, we postulate that

$$\begin{aligned} \sigma_a(1) &= f(t-t_0) e^{i\vec{k} \cdot \vec{r}_1} v(\vec{P}_1, \vec{k}), \\ S(12) &\equiv \frac{1}{2} [\sigma_{aa}(12) + \sigma_{ab}(12)] \\ &= f(t-t_0) e^{i\vec{k} \cdot (\vec{r}_1 + \vec{r}_2)/2} X(12; \vec{k}). \end{aligned} \quad (2)$$

This postulate and the sum rules impose certain conditions on the functions $v(\vec{P}_1, \vec{k})$ and $X(12; \vec{k})$. Following the arguments given by Stillinger and

Suplinskas,¹ we find that $v(\vec{P}_1, \vec{k})$ must be invariant when both $\vec{k} \rightarrow -\vec{k}$ and $\vec{P}_1 \rightarrow -\vec{P}_1$. Similarly $X(12; \vec{k})$ is invariant when $\vec{k} \rightarrow -\vec{k}$, $\vec{P}_1 \rightarrow -\vec{P}_1$, and $\vec{r}_{12} \rightarrow -\vec{r}_{12}$. As the system of interest is a fluid, there is the further restriction that $v(\vec{P}_1, \vec{k})$ must be cylindrically symmetric about an axis determined by the vector \vec{k} and that $X(12; \vec{k})$ must have cylindrical symmetry about this same axis for simultaneous rotation of its argument vectors \vec{P}_1 , \vec{P}_2 , and \vec{r}_{12} .

Introducing (2) into the first hierarchy equation, we find that⁶

$$\begin{aligned} (-k^2 D + i\vec{k} \cdot \vec{P}_1) v(1) \\ = n \int d\vec{\xi}_2 \varphi(2) g(r) U_{12} e^{i\vec{k} \cdot \vec{r}_{21}/2} X(12; \vec{k}), \end{aligned} \quad (3)$$

where

$$U_{12} = \nabla_1 u(12) \cdot (\partial_1 - \vec{P}_1), \quad (4)$$

$d\vec{\xi} \equiv d\vec{P} d\vec{r}$ and $\partial_i \equiv \nabla_{P_i}$.⁷ To first order in a wave-vector expansion, which is equivalent to Navier-Stokes hydrodynamics, the momentum-dependent part of $\sigma_a(1)$ is

$$v(1) = 1 - i\vec{k} \cdot \vec{P}_1 A(\frac{1}{2} P_1^2) + \dots, \quad (5)$$

which with (3) is sufficient to determine the self-diffusion coefficient

$$D = \frac{1}{3} \int dP_1 \varphi(1) P_1^2 A(\frac{1}{2} P_1^2); \quad (6)$$

the momentum average of the right-hand side of (3) is zero because of the structure of the operator U_{12} . Thus $A(\frac{1}{2} P^2)$ determines both D and the hydrodynamically significant part of the one-particle RDF.⁸

Within the DSA, the second hierarchy equation, which determines the partially species-averaged doublet function $S(12)$, is⁹

$$\left(\frac{\partial}{\partial t} + L_2 \right) S(12) - \nabla_1 w \cdot \partial_1 \sigma_a(1) = n K(12; 3) S(12), \quad (7)$$

where

$$L_2 = \vec{P}_1 \cdot \nabla_1 + \vec{P}_2 \cdot \nabla_2 - \nabla_1 w \cdot \partial_{12}, \quad (8)$$

$$K(12; 3) = \int d\vec{\xi}_3 \varphi(3) \left(\frac{(U_{13} + U_{23})g_3(123)}{g(12)} - U_{13}g(13) \right), \quad (9)$$

and $w(r)$ is the potential of mean force, $w = -\ln g$. The formal solution of (7) is

$$S(12; t) = O_t S(12; 0) + \int_0^t d\tau O_\tau [\nabla_1 w \cdot \partial_{12} \sigma_a(1; t - \tau) + nK(12; 3) S(13; t - \tau)] \quad (10)$$

in which the dynamical operator $O_t = e^{-tL_2}$. The effective potential in this Liouville operator reflects the details of the fluid structure and is both density and temperature dependent. Since $w(r)$ is oscillatory, reflecting the oscillations in $g(r)$, there are regions of this two-particle phase space for which the dynamical operator O_t has periodic solutions. These bound states should not be confused with the quasi-bound-states of a real fluid in which a particle may be trapped for the duration of many collisions within a "cage" formed by other particles. The oscillatory behavior of O_t presumably arises because we reduced a problem of N -body dynamics to one of two-body dynamics when we introduced the DSA. In that sense it is a nonphysical phenomenon and, as we shall see, one that does not affect the calculation of D or $A(\frac{1}{2}P_1^2)$. The period of oscillation for these phase points is $\tau_{\text{osc}}(\vec{r}_{12}, \vec{P}_{12})$. Most regions of phase space lead to scattering with an interaction time $\tau_{\text{int}}(\vec{r}_{12}, \vec{P}_{12})$. Both of these times are short, $\sim l/c$, where l is the range of $w(r)$ and c is the mean thermal speed of the molecules. Except for a vanishingly small set of phase points both of these times are much less than the hydrodynamic relaxation time $(k^2D)^{-1}$. As the operator O_τ in the integral of (10) acts on functions which vanish unless \vec{r}_{12} is small [we assume $w(r)$ has a finite range⁹], the upper limit in the integral is quite arbitrary for scattering events. For particles initially well separated, the properties of $w(r)$ ensure that $S=0$ is a solution. For bound states we accept a degree of ambiguity and choose an upper limit less than τ_{osc} which indicates that (10) cannot accurately describe $S(12; t)$ at all points in the two-particle phase space. The upper limits are designated as t^* . Due to the way in which the initial concentration wave is set up, $S(12; 0) = 0$ for self-diffusion and we may solve (10). Sub-

stituting from (2) and (5), we find that in the Navier-Stokes domain,

$$X(12; \vec{k}) = \int_0^{t^*} d\tau e^{-i\vec{k} \cdot (\vec{r}_1 + \vec{r}_2)/2} f(-\tau) O_\tau \times [\nabla_1 w \cdot \partial_{12} e^{i\vec{k} \cdot \vec{r}_1} v(\vec{P}_1, \vec{k}) + nK(12; 3) e^{i\vec{k} \cdot (\vec{r}_1 + \vec{r}_3)/2} X(13, \vec{k})]. \quad (11)$$

In this form the fact that $X(12; \vec{k})$ is consistent with the symmetry conditions may be somewhat obscure. However, the properties of the operators (4), (8), and (9) ensure that these conditions are satisfied. Since $t^* \ll (k^2D)^{-1}$ and $t^* \ll (kc)^{-1}$, we may expand the k -dependent term and find, to lowest order in k ,

$$\vec{x}(12) = \int_0^{t^*} d\tau O_\tau [\nabla_1 w \cdot \partial_{12} \vec{P}_1 A(\frac{1}{2}P_1^2) + nK(12; 3)\vec{x}(13)], \quad (12)$$

where we have used (5) and the analogous expression

$$X(12) = -i\vec{k} \cdot \vec{x}(12) + \dots \quad (13)$$

This, when introduced into (3), leads to the restriction

$$\vec{P}_1 + n \int d\vec{\xi}_2 \varphi(2)g(r)U_{12}\vec{x}(12) = 0. \quad (14)$$

Using the definition of L_2 and O_τ an equivalent form for (12) is

$$\vec{x}(12) = [O_{t^*} - 1] \vec{P}_1 A(\frac{1}{2}P_1^2) + \int_0^{t^*} d\tau O_\tau nK(12; 3)\vec{x}(13). \quad (15)$$

To determine $A(\frac{1}{2}P^2)$ and circumvent the ambiguities in this expression for $\vec{x}(12)$, we multiply (14) by $\vec{P}_1 \varphi(1)G(\frac{1}{2}P_1^2)$ and integrate over \vec{P}_1 . Manipulations familiar in kinetic theory¹⁰ lead to

$$\langle G \rangle \equiv \int d\vec{P}_1 \varphi(1)P_1^2 G = -B + C, \quad (16)$$

where

$$B = n \int d\vec{P}_1 d\vec{P}_2 d\vec{b}_{21} \varphi(1)\varphi(2)P_{12}G\vec{P}_1 \cdot (\vec{x}_\infty - \vec{x}_{-\infty}),$$

$$C = n \int d\vec{P}_1 d\vec{\xi}_2 \varphi(1)\varphi(2)g(r) \times (\vec{x} \cdot \nabla_1 uG + \vec{x} \cdot \vec{P}_1 \nabla_1 u \cdot \vec{P}_1 G'). \quad (17)$$

To obtain (17) we carried out part of the \vec{r}_{21} integration by transforming to cylindrical coordinates with the axis in the direction of \vec{P}_{21} ; the coordinate along this axis is ζ and \vec{b}_{21} , the impact parameter, is perpendicular to this axis. The quantities $\vec{x}_{\pm\infty}$ are computed from (15) by

setting $\zeta = \pm\infty$. This can be done since the second term on the right-hand side of (15) is zero because $K(12;3)\vec{x}(13) \rightarrow 0$ when $\vec{r}_{12} \rightarrow \infty$. Since O_τ translates a phase point backward in time, we see that $[O_\tau \vec{P}_1]_{\zeta=-\infty} = \vec{P}_1$ while $[O_\tau \vec{P}_1]_{\zeta=+\infty} = \vec{P}_1^*$ where \vec{P}_1^* is the initial momentum which long after scattering becomes \vec{P}_1 . Thus

$$\vec{x}_{-\infty} = 0, \quad \vec{x}_{+\infty} = (\vec{P}_1^* A^* - \vec{P}_1 A). \quad (18)$$

We may eliminate C by means of the following considerations. In (2) we postulated forms for the singlet and doublet RDF's. Introducing these into the second hierarchy equation (7) and making use of (5) and (13), we find that an alternate specification of $\vec{x}(12)$ is

$$L_2 \vec{x}(12) - \nabla_1 w \cdot \partial_1 [\vec{P}_1 A (\frac{1}{2} P_1^2)] = n K(12;3) \vec{x}(13), \quad (19)$$

a result well known from other approaches using the BBGKY hierarchy.^{1,3} Since L_2 and $K(12;3)$ have the same momentum parity, $\vec{x}(12)$ is odd in momentum because the inhomogeneous term is even in momentum. Thus we find that all terms in C integrate to zero and we may rewrite (16)

$$\langle G \rangle = n \int d\vec{P}_1 d\vec{P}_2 d\vec{b}_{21} \varphi(1)\varphi(2) \times P_{12} G \vec{P}_1 \cdot (\vec{P}_1 A - \vec{P}_1^* A^*), \quad (20)$$

where

$$\vec{P}_1^* A^* = \{e^{-\tau L_2} [\vec{P}_1 A (\frac{1}{2} P_1^2)]\}_{\zeta=+\infty}. \quad (21)$$

The integral in (20) is not dependent upon the nature of the bound states.

It is important to recognize that the various expressions for $\vec{x}(12)$ [Eqs. (12), (15), and (19)] are equivalent. This is easily seen for scattering states by substituting (12) into (19) and noting that both $O_\tau K(12;3)\vec{x}(13)$ and $O_\tau \nabla_1 w$ approach zero for large τ^* . For orbiting states these equations are only equivalent in a coarse-grained sense which is understandable since, in these cases, there is ambiguity in the choice of τ^* . As in the case of Eq. (11) the properties of the operators (4), (8), and (9) ensure that the symmetry constraints on $\vec{x}(12)$ are always satisfied.

Expanding A in terms of Sonine polynomials¹¹

$$A = \sum b_r S_{3/2}^{(r)} (\frac{1}{2} P_1^2) \quad (22)$$

and identifying G as $S_{3/2}^{(s)} (\frac{1}{2} P_1^2)$, we find from (16) and (20) that

$$3\delta_{s,0} = \sum Q_{sr} b_r, \quad (23)$$

where

$$Q_{sr} = n \int d\vec{P}_1 d\vec{P}_2 d\vec{b}_{21} \varphi(1)\varphi(2) \times P_{12} \vec{a}_s(1) \cdot (\vec{a}_r(1) - \{e^{-\tau L_2} [\vec{a}_r(1)]\}_{\zeta=+\infty})$$

with

$$\vec{a}_r(1) = \vec{P}_1 S_{3/2}^{(r)} (\frac{1}{2} P_1^2). \quad (24)$$

The coefficients b_r are then completely specified; by inverting the matrix Q and using (6), we find that

$$D = b_0 = 3(Q^{-1})_{00}, \quad (25)$$

which is precisely the Chapman-Enskog form for the self-diffusion coefficient. By approximating Q as an $n \times n$ matrix, we generate the form of the n th Chapman-Enskog approximation to D . The difference between (24) and the Chapman-Enskog formula arises from the scattering operator $e^{-\tau L_2}$ where L_2 is defined in (8); the results are only identical at low density where the potential of mean force can be replaced by the intermolecular potential.

Our results are exceptionally simple. The major features upon which our conclusions are founded are (a) imposition of asymptotic forms for the perturbation functions, Eq. (2); (b) construction of a Bogoliubov type of solution to the second hierarchy equation which, because of DSA, provides the closed form, Eq. (11), with dynamics governed by the effective Liouville operator L_2 ; (c) limitation to the Navier-Stokes domain which leads ultimately to Eq. (15); (d) recognition that the asymptotic solution in the hydrodynamic domain is also a solution of Eq. (19). In this manner we have constructed a closed form containing no adjustable parameters which may be used to compute the self-diffusion coefficient of a dense fluid. Since the time-evolution operator involves the potential of mean force, the structure of the fluid is intimately related to the transport coefficient of interest.

It is now clear why previous approaches based upon the hierarchy have been unsuccessful. Expansions in terms of the wave vector introduce no difficulties. The DSA is misleading for the regions of phase space which correspond to bound states with the effective Liouville operator L_2 . Previous work could not circumvent these domains which do not matter here. Finally, the resultant form for $\vec{x}_{+\infty}$ indicates that expansions of this function in terms of products of functions of \vec{P}_1 and \vec{P}_2 would be likely to converge very slowly. In earlier work functions analogous to $\vec{x}(12)$ were expanded in just such a way.¹⁻³

Whether this formalism can yield good practical estimates of D awaits numerical computation. Certain qualitative features are encouraging. The

first approximation to (25) is

$$D = \frac{3}{8} \frac{(\pi m k T)^{1/2}}{\pi \sigma^2 \rho} \frac{1}{\Omega^*(1, 1)}, \quad (26)$$

where σ is a range parameter for the potential and $\Omega^*(1, 1)$ is a collision integral familiar in kinetic theory.¹² As we increase the density of a gas, the range of the potential of mean force increases so that our theory correctly predicts that ρD decreases as gas density increases. Lowering temperature accentuates both maxima and minima in $w(r)$; calculations of $\Omega^*(1, 1)$ for various intermolecular potentials indicate that such changes increase $\Omega^*(1, 1)$.^{13,14} Thus D/\sqrt{T} decreases when T decreases, a trend observed in simple liquids.¹⁵

We now wish to show that our theory leads to results which are an improvement over a simple application of the Chapman-Enskog method to liquids. From experiments on a series of simple liquids Nagizadeh and Rice¹⁵ showed that the data on D could be reduced to corresponding states form with two parameters; for argon the characteristic length and energy are $\sigma = 3.418 \times 10^{-8}$ cm and $\epsilon = 1.71 \times 10^{-14}$ erg. For $T = 90^\circ\text{K}$ and $\rho = 1.374$ g cm⁻³ they found $D = 2.43 \times 10^{-5}$ cm² sec⁻¹. To estimate the significance of using $w(r)$ instead of $u(r)$, we use the following procedure. If we describe argon as hard spheres with diameter σ we find from (25) that $D = D_0/\Omega^*(1, 1)$ where $D_0 = 12.0 \times 10^{-5}$ cm² sec⁻¹. To estimate $\Omega^*(1, 1)$ consider $w(r)$ for a hard-sphere fluid. The calculations of Alder and Hecht¹⁶ allow us to estimate an effective well depth by comparing the values of $g(r)$ at the first maximum and minimum; we use this procedure because minima in $g(r)$ should accentuate the properties of a potential well. At the density of interest which is 1.7 times the close-

packed volume, we find that $\beta\Delta w = 1.84$ which corresponds to the reduced temperature, $T^* = 0.54$. Calculations for a variety of intermolecular potentials suggest that, depending upon the details of the potential, $\Omega^*(1, 1)$ is between 2 and 4 at this T^* .^{13,14} This suggests that our approach will lead to a value of D in the vicinity of $(3-6) \times 10^{-5}$ cm² sec⁻¹, which is quite close to the observed value. In contrast, simple Chapman-Enskog theory leads to the result $D = D_0$; application of Enskog-dense gas theory¹⁷ to liquid argon in the state of interest yields negative values of D . While these observations are encouraging, only a direct comparison of a measured D with one computed from this theory using an experimental $g(r)$ can provide a true test. Naturally the "experimental" input can be obtained from a computer simulation instead of laboratory data. These complex numerical studies are being undertaken.

This work, based upon the DSA, provides a direct link between the structure of a fluid and the self-diffusion coefficient. Suitably modified, it should be applicable to ordered phases as well as fluids. We are presently trying to extend these ideas to treat other transport phenomena. It is already clear that expressions for the shear viscosity, thermal conductivity, etc. will be quite different. The leading term in the singlet perturbation functions is now momentum dependent. When the proper momentum average of (3) is taken to determine a transport coefficient the terms that depend upon $X(12; \vec{k})$ do not vanish. It appears that we will have to determine both singlet and doublet perturbation functions as well as know the intermolecular potential to be able to extend our treatment.

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⁴This is the nonequilibrium analog to the Kirkwood superposition approximation.

⁵See Ref. 1 for a discussion of this procedure.

⁶The derivation is given in Sec. II of Ref. 3.

⁷Units are chosen so that $m = k_B T = 1$.

⁸This is a well-known result in kinetic theory.

⁹This will not be true near the critical point.

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