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A self-consistent theory of single-particle motion in ordinary and supercooled liquids

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Abstract. The mean square displacement of a tagged particle in a liquid is known to exhibit a diffusive linear time dependence beyond a microscopic timescale. By making use of simple mode-coupling concepts we derive a set of analytic self-consistent equations for the relevant dynamical quantities in this regime, namely the diffusion coefficient and the intercept. The results of the theory are successfully compared with the data obtained by simulation experiments in different systems.

1. Introduction

In the last decade considerable progress has been made towards a better understanding of the physical mechanisms behind the dynamics of simple liquids [1]. An important step has been the recognition that time-dependent correlations in a dense system are controlled by *two* kinds of dynamical processes in their associated memory functions. The first one is due largely to uncorrelated, short-range interactions, which in a hard sphere fluid can be essentially identified with binary encounters. In all cases these events induce a fast decay mechanism, which even in a system with continuous potential we shall simply refer to as due to 'binary' collisions. In contrast, the second process stems from non-linear couplings of the variable of interest with collective and slowly varying dynamical 'modes'. A rigorous treatment of both effects requires a combined use of concepts from kinetic and mode-coupling theories [2]. In the latter framework equilibrium properties are assumed to be known; even so, the final output of the general theory for the dynamics is a set of non-linear integro-differential equations which make even a numerical solution quite difficult to obtain.

In some cases, however, a much simpler treatment appears possible by introducing physical approximations which still retain the essential features of the processes and lead to rather good quantitative predictions. One example is a simplified mode-coupling theory of the glass transition [3]. More recently, the anomalous increase of the de Gennes slowing down of the density autocorrelation in a supercooled liquid has also been interpreted along similar lines [4]. The simplicity of these approaches and the reliability of their results stimulate the need for such investigations of other basic quantities in liquid state dynamics. Here, we show that the most important features of single-particle motion in a monatomic liquid can indeed be predicted by a rather simple approach in which, nevertheless, phenomenological arguments are kept to a minimum.

The format of the paper is as follows. The next section introduces the mean square displacement of a particle in a liquid and through its linear asymptotic behaviour, formal expressions for the slope (i.e. the diffusion coefficient) and the intercept. These are given in terms of a memory function whose components are analysed separately, and lead to equations which are solved self-consistently in section 3. Specific results are obtained for liquid rubidium and argon.

2. General framework

Let us consider the mean square displacement $\delta r^2(t) \equiv \langle [\boldsymbol{r}_1(t) - \boldsymbol{r}_1(0)]^2 \rangle$ of a tagged particle in the liquid. This can be expressed in terms of the normalised velocity autocorrelation function $\varphi(t) = \langle \boldsymbol{v}_1(0) \cdot \boldsymbol{v}_1(t) \rangle / \langle v_1^2 \rangle$ by

$$\delta r^2(t) = (6k_B T/m) \int_0^t \mathrm{d}\tau \, (t - \tau)\varphi(\tau). \tag{1}$$

Beyond a microscopic time, t_0 (typically, ~1 ps in simple liquids), (1) leads to the linear diffusive behaviour $\delta r^2(t) = 6Dt + I$, where D is the diffusion coefficient and I the intercept of the straight line extrapolated at $t = 0$. The validity of the diffusive law follows from the rapid decay of $\varphi(t)$ for $t < t_0$; in principle, $\varphi(t)$ is also predicted to have a slower long time tail ($\propto t^{-3/2}$), but its amplitude in the liquid range is very small and its effect can safely be neglected. In such a case the Laplace transform $\hat{\varphi}(z) = \int_0^\infty \mathrm{d}t \, \mathrm{e}^{-zt} \varphi(t)$ is analytic near $z = 0$, and

$$D = (k_B T/m)\hat{\varphi}(z = 0) \qquad I = -(6k_B T/m) \int_0^\infty \mathrm{d}\tau \, \tau\varphi(\tau). \tag{2}$$

Introducing the memory function, $K(t)$, associated with $\varphi(t)$ and defined by $\hat{\varphi}(z) = [z + \hat{K}(z)]^{-1}$, (2) can be written as

$$D = k_B T/m\hat{K}(z = 0) \qquad I = (6mD^2/k_B T)\left(\int_0^\infty \mathrm{d}\tau \, \tau K(\tau) - 1\right). \tag{3}$$

The memory function is the central quantity in the following analysis. Using many-body techniques we may formally express $K(t)$ in the form [5]

$$K(t) = K_B(t) + K_{MC}(t) \tag{4}$$

where the fast contribution $K_B(t)$ is associated with 'binary' collisions, whereas the 'mode-coupling' part $K_{MC}(t)$ is represented in terms of slowly varying collective variables.

2.1. The binary component

At very short times $K(t) \approx K_B(t)$; in particular, $K(0) = K_B(0) = \Omega_0^2$, where the Einstein frequency Ω_0 defined by

$$\Omega_0^2 = (n/3m) \int \mathrm{d}\boldsymbol{r} \, \nabla^2 \varphi(r) \, g(r) \tag{5}$$

is expressed in terms of the interatomic potential, $\varphi(r)$, and of the radial distribution function, $g(r)$, for a liquid with number density n. Moreover, both $K(t)$ and $K_B(t)$ have the same initial decay time

$$\tau_B = [|\ddot{K}(0)|/2K(0)]^{-1/2} \tag{6}$$

where $\ddot{K}(0)$ can straightforwardly be written as ($r^\alpha = x, y, z$)

$$\ddot{K}(0) = -(2n/m^2)\sum_\alpha \int \mathrm{d}\boldsymbol{r} \left(\frac{\partial^2\varphi(r)}{\partial x\,\partial r^\alpha}\right)^2 g(r) - (n/m)^2 \sum_\alpha \int\int \mathrm{d}\boldsymbol{r}\,\mathrm{d}\boldsymbol{r}' \frac{\partial^2\varphi(\mathrm{r})}{\partial \mathrm{x}\,\partial \mathrm{r}^\alpha}\frac{\partial^2\varphi(\mathrm{r}')}{\partial \mathrm{x}'\,\partial \mathrm{r}'^\alpha}[\mathrm{g}^{(3)}(\boldsymbol{r},\boldsymbol{r}') - g(r)g(r')]. \tag{7}$$

Even if in principle the presence of the triplet distribution $g^{(3)}(\boldsymbol{r},\boldsymbol{r}')$ in the second term on the RHS appears to complicate the evaluation of τ_B, in practice the square bracketed factor in this term greatly decreases its relevance with respect to the pair contribution with a single $g(r)$. This expectation is supported by numerical calculations: for example, in ordinary liquid rubidium at 318 K (where the effective potential found by Price *et al* [6] provides a good description of structural properties), we find that the first term on the RHS of (7) eventually leads to $\tau_B = 0.194$ ps, to be compared with the full value $\tau_B = 0.217$ ps obtained in [5] by a superposition approximation for $g^{(3)}$. In liquid Rb, this decay time is found to be virtually unchanged even in the supercooled region [7]. On the other hand, in Lennard-Jones liquid 'argon' τ_B is found to be 0.122 ps [5]. Decay times of this order are much shorter than the diffusive timescales, which typically comprise several picoseconds. We therefore assume that $K_B(t) \approx \Omega_0^2 f(t/\tau_B)$, where the scaling function $f(x)$ is an even and rapidly decaying quantity, such that $f(x \to 0) \approx 1 - x^2$. Appropriate choices are $f(x) = \exp(-x^2)$ or $f(x) = \mathrm{sech}^2 x$ and lead to results for $D_B \equiv (k_B T/m)\,(\int_0^\infty \mathrm{d}t\, K_B(t))^{-1}$ which have only slightly different numerical factors. Here, we use $f(x) = \mathrm{sech}^2 x$ which gives

$$D_B = k_B T/m\Omega_0^2 \tau_B. \tag{8}$$

There is an alternative derivation of the decay time τ_B, which for two reasons can usefully be considered. The first is that the application of the superposition approximation is avoided completely, and the second that the nature of the short-range interaction, thought to be responsible for the rapid decay of $K_B(t)$, is emphasised. It proceeds by identifying D_B with the Enskog binary collision expression for the diffusion coefficient, given by

$$D_E = (3/8)(k_B T/\pi m)^{1/2}(n\sigma_{HS}^2 g(\sigma_{HS}))^{-1} \tag{9}$$

$g(\sigma_{HS})$ being the contact value of $g(r)$ and σ_{HS} the sphere diameter. A value for D_E is obtained here by treating the liquid as a rigid sphere fluid with an appropriately defined sphere diameter. There is clearly some ambiguity in the choice for the latter, denoted by $\sigma_{HS}(T)$ to emphasise its expected temperature dependence. A realistic choice can be made on the basis of the penetration depth achieved by an atom with the average thermal energy $\frac{3}{2}k_B T$. For values of r smaller than that of the principal minimum in $\varphi(r)$, the potential is repulsive. If ε is the depth of the minimum, we select a value for $\sigma_{HS}(T)$ through the condition

$$\varphi(r = \sigma_{HS}(T)) + \varepsilon = \tfrac{3}{2}k_B T. \tag{10}$$

The contact value, $g(\sigma_{HS}(T))$, is then obtained from the rigid sphere radial distribution

Table 1. Theoretical diffusion coefficients D (units 10^{-5} cm^2 s^{-1}) and intercepts $\bar{I} = I/\sigma^2$ compared with the corresponding data found by computer simulations (CS) in three model systems†: Rb 318 (ordinary liquid rubidium, $n\sigma^3 = 0.905$, $T = 318$ K; CS [9]), Rb 270 (supercooled liquid rubidium, $n\sigma^3 = 0.905$, $T = 270$ K; CS [9]) and Ar (Lennard-Jones liquid argon, $n\sigma^3 = 0.844$, $T = 86.5$ K; CS [8]).

	Rb 318	Rb 270	Ar
D_B	3.84	3.26	2.47
D	2.46	1.57	1.50
D (CS)	2.41	1.49	1.75
$\bar{I}_B$	0.003	0.002	−0.007
$\bar{I}$	0.045	0.056	0.042
$\bar{I}$ (CS)	0.047	0.045	0.031

† From the CS structural data one deduces the following values of the parameters: Ω_0^2 (ps^{-2}) = 36.92, 36.55, 59.29; $\Gamma = 233$, 273, 385; $A\sigma = 1.74$, 2.5, 1.5; $c/\Omega_0^2 = 0.289$, 0.355, 0.168 and $\gamma/\Omega_0 = 0.064$, 0.046, 0.048 where the entries refer to Rb 318, Rb 270 and Ar, respectively. In all cases, $q_m\sigma \approx 6.8$. Letting $t_0 = 2\pi/\Omega_0$, the quantities $\lambda(t_0)$ and $\mu(t_0)$ defined in the text turn out to be $\lambda(t_0) = 62$, 87, 66; $\mu(t_0) = 1600$, 2610, 1666.

function, at a packing fraction $\pi = (\pi/6)n\sigma_{HS}^3(T)$. For liquid rubidium at 318 K we find $\sigma_{HS}(T) \approx 4.35$ Å, $D_B = 3.86 \times 10^{-5}$ cm^2 s^{-1} and hence $\tau_B = 0.216$ ps (using (8) and a value for the Einstein frequency given in table 1). In the supercooled region $\sigma_{HS}(T) \approx 4.405$ Å, $D_B = 3.19 \times 10^{-5}$ cm^2 s^{-1} and $\tau_B = 0.222$ ps. These relaxation times are in excellent agreement with the predictions based on the initial decay of the memory function. This is also the case in liquid argon. For $T = 86.5$ K and $n = 0.0214 \times 10^{24}$ cm^{-3}, the results are $\sigma_{HS}(T) \approx 3.39$ Å, $D_B = 2.63 \times 10^{-5}$ cm^2 s^{-1} and $\tau_B = 0.115$ ps.

Whichever the way to estimate τ_B and D_B, the basic physical conclusion is that the purely binary model ($K(t) = K_B(t)$ at all times) is unable to account for the values of the diffusion coefficient and of the intercept actually observed in liquids. More precisely, the binary predictions

$$D_B = k_B T/m\Omega_0^2\tau_B \qquad I_B = 6(mD_B^2/k_B T)(\Omega_0^2\tau_B^2 \ln 2 - 1) \tag{11}$$

are found to be in severe disagreement with the simulation data for typical simple liquids near the triple point (see table 1 where the values refer to τ_B evaluated according to (6) and (7)). Note that for the supercooled system the discrepancies are even more pronounced.

2.2. The mode-coupling component

The important consequence of the previous results is that the presence of a slowly varying part in $K(t)$ is essential, as indeed was found several years ago on a purely phenomenological basis [8]. The actual form of these long-lasting features can be established by the mode-coupling theory. A complete account is quite involved and would be inappropriate here. The details are given, for example, in [5]. In principle, several modes should be included in the analysis (density and current density fluctuations, etc). However, in the liquid range the slowness of structural relaxation makes the density fluctuations (self or collective) the most important decay channel. Their contribution to the decay of $K(t)$ can be written as [5]:

$$K_{\mathrm{MC}}(t) = (nk_{\mathrm{B}}T/24\pi^3 m)\int \mathrm{d}\boldsymbol{q}\, q^2c^2(q)(F_{\mathrm{s}}(q,t) - F_0(q,t))F(q,t). \tag{12}$$

Here $c(q)$ is the direct correlation function, $F(q,t)$ the intermediate scattering function, $F_{\mathrm{s}}(q,t)$ its self part and $F_0(q,t) = \exp(-k_{\mathrm{B}}Tq^2t^2/2m)$ the free particle limit common to both F and F_{s}. Note that $K_{\mathrm{MC}}(t\to 0) \propto t^4$, thereby confirming that the initial time decay of $K(t)$ is dominated by the purely 'binary' contribution.

Mode-coupling methods were developed to treat long-lasting decay processes. Therefore, in the wavevector integral above, particular relevance should be given to the most slowly varying density modes, thereby permitting a further simplification of the analysis. In the liquid range the effect of the $q \to 0$ hydrodynamic wavevectors is negligible (even for long times, where they yield a higher-order 'tail'). The dominant contribution is provided instead by the slow de Gennes modes $F(q \approx q_{\mathrm{m}}, t)$, where q_{m} is the position of the main peak of the structure factor $S(q)$. Thus, we argue that (12) can be approximated as

$$K_{\mathrm{MC}}(t) \approx c(F_{\mathrm{s}}(q_{\mathrm{m}},t) - F_0(q_{\mathrm{m}},t))F(q_{\mathrm{m}},t)/S(q_{\mathrm{m}}) \tag{13}$$

where $c = Ak_{\mathrm{B}}Tq_{\mathrm{m}}^4/6nm\pi^2$, $A = \int_{(q_{\mathrm{m}})}\mathrm{d}q\, h(q)$ being the area under the main peak of $h(q) = S(q) - 1$. Formally, the result (13) is obtained by making use of the identity $nc^2(q)F(q,t) = h(q)c(q)F(q,t)/S(q)$ along with the simplification $h(q) = A\delta(q - q_{\mathrm{m}})$ (which implies $nc(q_{\mathrm{m}}) = 1$) to emphasise the dominance of the contribution around the principal peak as far as the dynamics is concerned [3]. Equation (13) has been demonstrated to be in quantitative agreement with previous computer simulation (CS) data for liquid rubidium [9].

It is worthwhile to stress at this stage that the magnitude of $K_{\mathrm{MC}}(t)/\Omega_0^2$ in different liquids depends ultimately on the factor

$$c/\Omega_0^2 = [(q_{\mathrm{m}}\sigma)^4A\sigma/6\pi^2n\sigma^3](1/\Gamma) \tag{14}$$

where σ is the usual length associated with the pair potential and $\Gamma = m\Omega_0^2\sigma^2/k_{\mathrm{B}}T$. For example, in liquid argon this magnitude is predicted to be distinctly smaller than in liquid rubidium: indeed, whereas the square-bracketed factor in (14) is about the same, Γ is nearly doubled in argon because of the larger value of Ω_0^2 (in turn, due to the steeper repulsive potential in this system).

To be consistent, the intermediate scattering function $F(q_{\mathrm{m}}, t)$ in (13) should be evaluated by considering in its memory function both fast and slow contributions. This procedure has successfully been applied [3, 4] to situations of marked slowing down of F, including the possibility of structural arrest. If, however, we limit ourselves to ordinary and moderately supercooled liquids, fairly good results for $F(q_{\mathrm{m}}, t)$ are obtained by neglecting mode-coupling effects [10]. A typical example of such a theory is the well known viscoelastic model [11]. For $q \approx q_{\mathrm{m}}$ the result can approximately be written as:

$$\begin{aligned} F(q_{\mathrm{m}},t) &= S(q_{\mathrm{m}})\exp[-(2\Omega^2(q_{\mathrm{m}})/\sqrt{\pi})(\Omega_{\mathrm{L}}^2(q_{\mathrm{m}}) - \Omega^2(q_{\mathrm{m}}))^{-1/2}t] \\ &\equiv S(q_{\mathrm{m}})\exp(-\gamma t). \end{aligned} \tag{15}$$

Here $\Omega^2(q_{\mathrm{m}}) = k_{\mathrm{B}}Tq_{\mathrm{m}}^2/mS(q_{\mathrm{m}})$, and $\Omega_{\mathrm{L}}^2(q_{\mathrm{m}})$ is defined in terms of the fourth frequency moment of the dynamic structure factor [11]. The use of the above expression for $F(q_{\mathrm{m}}, t)$

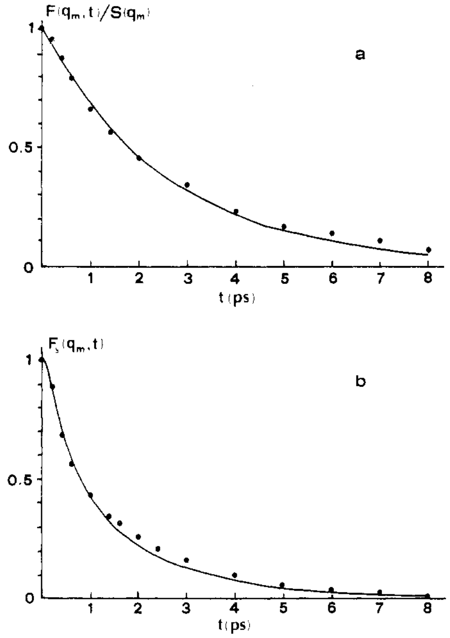

Figure 1. (*a*) Normalised intermediate scattering function for liquid Rb at 318 K and $q_m\sigma = 6.75$. The full curve is the result from (15) and the dots are our simulation data. (*b*) Self-intermediate scattering function for liquid Rb at 318 K and $q_m\sigma = 6.75$. The full curve is the Gaussian approximation (16), the dots are our simulation data.

has a clear perturbative character in the present context. Moreover, the discrepancies of (15) are found to occur at rather long times [4, 9], where $K_{\mathrm{MC}}(t)$ is very small.

The last step is the specification of $F_s(q_m, t)$ in (13). We have adopted the Gaussian approximation

$$F_s(q_m,t) = \exp(-\tfrac{1}{6}q_m^2\,\delta r^2(t)). \tag{16}$$

Non-Gaussian corrections are indeed small for ordinary liquids; their relevance increases only for strongly quenched systems [12]. Thus, both (15) and (16) have approximately the same range of applicability, comprising ordinary and moderately supercooled liquids. The validity of the approximations behind (15) and (16) is demonstrated in figure 1.

3. Results and discussion

The presence of $\delta r^2(t)$ in (16) paves the way for a *self-consistent* evaluation of the quantities D and I. To demonstrate this, we write (3) in a form in which the non-binary contributions are made explicit:

$$D = \left(D_{\mathrm{B}}^{-1} + (m/k_{\mathrm{B}}T)\int_0^\infty \mathrm{d}\tau\, K_{\mathrm{MC}}(\tau)\right)^{-1} \tag{17a}$$

$$I = I_{\mathrm{B}} + [(D/D_{\mathrm{B}})^2 - 1]I_{\mathrm{B}} + 6(m/k_{\mathrm{B}}T)D^2\int_0^\infty \mathrm{d}\tau\, \tau K_{\mathrm{MC}}(\tau). \tag{17b}$$

As already remarked, beyond the microscopic time t_0 (typically ≈ 1 ps), $\delta r^2(t)$ can be approximated as $6Dt + I$. As a consequence, the integrals involving $K_{\mathrm{MC}}(\tau)$ are evaluated analytically for $\tau > t_0$. This time has been taken as $t_0 = 2\pi/\Omega_0$, a choice consistent with the physical meaning of the Einstein frequency. In this time range, $F_0(q_{\mathrm{m}}, \tau)$ is nearly negligible, and introducing the dimensionless quantities $\tilde{D} = D/\sigma^2\Omega_0$, $\tilde{I} = I/\sigma^2$ we obtain:

$$\tilde{D}^{-1} = \tilde{D}_{\mathrm{B}}^{-1} + \lambda(t_0) + (\Gamma c/\Omega_0^2)\exp\{-[(q_m\sigma)^2\tilde{I}/6 + B(\tilde{D})\Omega_0 t_0]\}/B(\tilde{D}) \tag{18a}$$

$$\tilde{I} = \tilde{D}^2\{(\tilde{I}_{\mathrm{B}}/\tilde{D}_{\mathrm{B}}^2) + \mu(t_0) + 6[\tilde{D}^{-1} - \tilde{D}_{\mathrm{B}}^{-1} - \lambda(t_0)][\Omega_0 t_0 + B(\tilde{D})^{-1}]\}. \tag{18b}$$

Here $B(\tilde{D}) = (q_{\mathrm{m}}\sigma)^2\tilde{D} + (\gamma/\Omega_0)$; moreover,

$$\lambda(t_0) = (\Gamma/\Omega_0)\int_0^{t_0} \mathrm{d}\tau\, K_{\mathrm{MC}}(\tau) \qquad \mu(t_0) = 6\Gamma\int_0^{t_0} \mathrm{d}\tau\, \tau K_{\mathrm{MC}}(\tau) \tag{19}$$

are the mode-coupling contributions coming from the time interval $(0, t_0)$, where the mean square displacement has not yet reached the diffusive regime. Although for an accurate evaluation of D and I the quantities (19) cannot be neglected, the dominant correction to the binary results is provided by the diffusive $\tau > t_0$ contributions. Thus, even a relatively rough evaluation of $\lambda(t_0)$ and $\mu(t_0)$ is sufficient. For example, for $0 < \tau < t_0$ one may choose the simple empirical form $K_{\mathrm{MC}}(\tau) = b\tau$, with the constant, b, determined so that bt_0 coincides with the actual memory function (13) at $\tau = t_0 = 2\pi/\Omega_0$. A more precise evaluation of the quantities (19) has also been made by carrying out the integrals numerically. To do this, CS data were used in F_{s} for $\delta r^2(t)$. These data are available for ordinary and supercooled liquid rubidium [9] and for Lennard-Jones liquid 'argon' [8]. The results reported in table 1 refer to this more accurate evaluation. However, nearly the same results are obtained by the 'empirical' method which, e.g., predicts $D = 2.503 \times 10^{-5}$ cm^2 s^{-1} and $I/\sigma^2 = 0.044$ for ordinary liquid Rb at 318 K.

Since all the other non-binary parameters appearing in (18) are deducible from purely structural data, we finish with a set of self-consistent equations to be solved for the unknown quantities D and I. The values eventually found for D and I are reported in table 1 for the three systems already mentioned, along with the corresponding 'exact' CS data. In all cases the predictions for both D and I are a marked improvement with respect to the binary values, and the overall comparison with the CS findings appears to be quite satisfactory, especially for the supercooled Rb state where the binary results were particularly poor.

An alternative to the procedure of splitting the time integrals in (17) into two regions, defined by the introduction of t_0, is discussed in the appendix. This makes use of an expression for the mean square displacement, derived from (1) with a simple model for $\varphi(t)$. The latter is derived from an exponential memory function (see [1], p 212), which at least qualitatively describes the features of the velocity autocorrelation function observed in CS data of dense liquids. Even by this alternative procedure, the results obtained for the diffusion coefficient and the intercept are found to be in quite good agreement with the CS findings.

In conclusion, our aim has been to develop a reliable means of calculating the self-diffusion coefficient in a simple liquid, given some limited information about the static structural properties. The relative simplicity of our results is due to the relevance of the mode-coupling decay channel associated with 'microscopic' density fluctuations with $q \approx q_{\mathrm{m}}$. In this sense, the theory extends to the 'self' case the validity of the previous works [3, 4] dealing with collective motion. There are, however, some exceptions, in which the complexity of the mode-coupling integrals cannot be bypassed in the way suggested here. A simple example is provided by the stress autocorrelation function, in which the coupling vertex involves the *derivative* of $c(q)$ [13]. Although a limited range of wavevectors about q_m is still extremely important, we cannot use the simplification adopted in the present case. The derivative of $c(q)$ clearly vanishes as $q \rightarrow q_m$ and a more appropriate treatment of the wavevector integral must be made. Finally, the self-consistent nature of our equations (implemented with a better treatment of F and F_s) suggests the possibility of investigating more closely the approach of the system towards a 'glassy' phase.

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Appendix

The need to split the time integral in (17*a*) and (17*b*) into two regions, by the introduction of the time $t_0 = 2\pi/\Omega_0$, may be avoided if a realistic expression for the mean square displacement could be constructed and used in the Gaussian model for $F_s(q_m, t)$. We suggest such an expression in this appendix, and compare the subsequent results for the diffusion coefficients with those in table 1. It is based on an assumed exponential time-dependence for the memory function $K(t)$ associated with the velocity autocorrelation function $\varphi(t)$ [1]. The latter is easily obtained and used to derive an analytic expression for $\delta r^2(t)$ by means of (1). The memory function contains two parameters, C and α, such that $K(t) = C\exp(-\alpha t)$. In [1], $C \equiv \Omega_0^2$ to guarantee the short-time behaviour of $\varphi(t)$, and the inverse relaxation time α is chosen so that the integrated value of $\varphi(t)$ correctly reproduces some predetermined value for D. The intercept value of the mean square displacement is clearly not guaranteed by this procedure, and to achieve this we prefer to have the flexibility in the selection of C. This different philosophy is also consistent with the importance of the intermediate- and long-time behaviour of the memory function, referred to in section 3.

Within this framework, the mean square displacement is eventually obtained as

$$\begin{aligned}\delta r^2(t) = (6k_B T/m)\{&\alpha t/C + (C-\alpha^2)/C^2 + \exp(-\alpha t/2)\\ &\times[(\alpha/2\varepsilon C^2)(\alpha^2 - 3C)\sin \varepsilon t - (C-\alpha^2)/C^2 \cos \varepsilon t]\}\end{aligned} \tag{A1}$$

where $\varepsilon = (C - \alpha^2/4)^{1/2}$. At sufficiently long times, $\delta r^2(t) \rightarrow 6Dt + I$, and to reproduce this asymptotic form we select

$$\alpha = mCD/k_B T \qquad I = (6k_B T/m)(C - \alpha^2)/C^2. \tag{A2}$$

Thus

$$C = [mI/6k_B T + (mD/k_B T)^2]^{-1}. \tag{A3}$$

Hence, in the present context, the more obvious choice of a value for C is sacrificed in favour of a correct asymptote. Unfortunately, even with this modification, the predicted mean square displacement has some features which are not apparent in the CS data. When used to predict $F_s(q_m, t)$ via (16), we obtain a result which tends to oscillate about the monotonic decay displayed by the computer data, before achieving the same asymptotic form.

Nevertheless, by means of (A2) and (A3), $F_s(q_m, t)$ is completely specified by selecting D and I. This result is used in (13) for $K_{MC}(\tau)$ and the values for D and I selected in a systematic fashion until (17*a*) and (17*b*) are simultaneously satisfied. In the units employed in table 1, the results are $D = 2.61$, 1.68 and 1.68; $\tilde{I} = 0.045$, 0.057 and 0.042 for Rb 318, Rb 270 and Ar, respectively.

Note added in proof. For the stress autocorrelation function, the more accurate analysis mentioned in the concluding remarks has now been completed by one of the authors [14].

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