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Does the Velocity Autocorrelation Function Oscillate in a Hard-Sphere Crystal?

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An approximate kinetic theory is used to compute the velocity autocorrelation function (VACF) in a hard-sphere crystal. In general the theory predicts that the VACF is oscillatory in time. However, in practice, near coexistence the oscillations will be difficult if not impossible to observe because by the time the oscillations occur the VACF has decayed almost to zero. At higher densities the theory predicts that the oscillations are probably just barely observable. In all cases the time integral of the VACF is zero.

KEY WORDS: Kinetic theory; velocity autocorrelation function; hard sphere crystal.

1. INTRODUCTION

In this paper I use hard-sphere kinetic theory to compute the velocity autocorrelation function (VACF) for a hard-sphere crystal. The calculation is based on the revised Enskog theory (RET) (see, e.g., ref. 1) for the crystal phase.(2) The motivation for using this approach and its limits of validity in the solid phase have been discussed elsewhere.(2) Basically, the RET is a mean field kinetic theory. In any phase it contains exact static properties. It is also exact in the high-dimensionality limit for all times and for short times in all dimensions. Therefore, in three-dimensional systems it is a qualitatively accurate theory when the physics is dominated by the short-time behavior and when there are no large long-time anomalies due to long-time tail effects and structural relaxation effects. Throughout this paper I assume that the RET is a reasonable first approximation theory in the solid state. Some additional remarks on this point are given in Section 3.

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The particular question addressed in this paper is whether or not the VACF oscillates in a hard-sphere crystal. For any smooth potential there is overwhelming evidence that the VACF always oscillates in the solid phase. For example, if the thermal vibrations in a crystal can be approximated by a harmonic theory, then the structure in the VACF is intimately related to the phonon spectrum (see, e.g., ref. 3). Even in standard simple fluids which interact through harsh, but continuous, potentials where a harmonic approximation is problematic there is ample evidence that in the solid phase the VACF will oscillate. Already in the dense fluid and supercooled fluid phases the VACF oscillates with a characteristic solidlike behavior at short times.(4,5) As the interparticle potential becomes softer, the oscillations in general become more pronounced.(6) An extreme case of a soft potential is the Yukawa fluid, which has been used as a model for colloids. For this fluid the VACF exhibits very pronounced oscillations.(7,8)

For hard-sphere crystals the situation is less clear. They are the most anharmonic solid conceivable. For example, standard expressions(3) for elastic coefficients do not exist for a hard-sphere crystal because the hard-sphere potential is not differentiable. To my knowledge there are no published molecular dynamics results which indicate that the VACF oscillates in dense, hard-sphere systems. Detailed comments on available computer experimental results will be given in Section 3. Using the RET, I give theoretical arguments that suggest that although in general the VACF oscillates in a hard-sphere crystal, in practice the oscillations will be difficult to detect. Structurally the RET leads to a harmoniclike equation for the VACF, but the magnitude of the damping term is comparable to the spring constant term. The net result is either overdamped or strongly damped oscillations in the VACF. I stress that these results are only suggestive because the RET is only an approximate equation. It is possible that more complicated correlation effects, which are neglected in the RET, could lead to more pronounced and longer-lived oscillations in the VACF in the hard-sphere crystal. Also note that if the calculations given here are qualitatively accurate, then whether or not the VACF oscillates in a hard-sphere crystal is a matter of detail and conceptually there is no difference between a hard-sphere crystal and other crystals as far as the VACF is concerned.

2. BASIC THEORY AND APPROXIMATE SOLUTION

In Section 2.1 the RET for self-correlations in a hard-sphere crystal is given. In Section 2.2 a low-order moment solution method is used to reduce the kinetic equation for the VACF to a differential equation in real space. In Section 2.3 this differential equation is approximately solved.

2.1. The Kinetic Equation

The revised Enskog kinetic equation for self-correlation functions in an equilibrium hard-sphere crystal is^(1)

$$[\partial_t + \mathbf{V}_1 \cdot \nabla_1]\, C_s(1t; 1') = \int d2\, \bar{T}_-(12)\, n_{\rm eq}(\mathbf{x}_2)\, \phi_{\rm eq}(V_2)\, G_2[\mathbf{x}_1, \mathbf{x}_2 \mid n_{\rm eq}]\, C_s(1t; 1') \tag{2.1a}$$

Here $1 = \mathbf{x}_1, \mathbf{V}_1$ is a point in μ space and C_s is the self-correlation function,

$$C_s(1t; 1') = \left\langle \sum_{i=1}^{N} \delta[\mathbf{x}_1 - \mathbf{r}_i(t)]\, \delta[\mathbf{V}_1 - \mathbf{v}_i(t)]\, \delta[\mathbf{x}_1' - \mathbf{r}_i]\, \delta[\mathbf{V}_1' - \mathbf{v}_i] \right\rangle \tag{2.1b}$$

where the angular brackets denote an equilibrium canonical ensemble average and $(\mathbf{r}_i, \mathbf{v}_i)$ is the phase of particle i in an N-particle system. In Eq. (2.1a), $n_{\rm eq}(\mathbf{x})$ is the thermally-averaged, spatially-dependent equilibrium number density in the crystal phase, $\phi_{\rm eq}(V)$ is the Maxwell distribution function in velocity space, and G_2 is related to the equilibrium spatial two-point distribution function f_2 by

$$f_2(\mathbf{x}_1, \mathbf{x}_2) = \theta(x_{12} - \sigma)\, n_{\rm eq}(\mathbf{x}_1)\, n_{\rm eq}(\mathbf{x}_2)\, G_2[\mathbf{x}_1, \mathbf{x}_2 \mid n_{\rm eq}] \tag{2.1c}$$

and it depends functionally on $n_{\rm eq}(\mathbf{x})$. Here $\theta(x) = 1$ for $x > 0$ and is zero otherwise. $\bar{T}_-(12)$ in Eq. (2.1a) is a hard-sphere collision operator that is given by^(9)

$$\bar{T}_-(12) = \sigma^2 \int d\hat{\boldsymbol{\sigma}}\, \theta(\mathbf{V}_{12} \cdot \hat{\boldsymbol{\sigma}})\, |\mathbf{V}_{12} \cdot \hat{\boldsymbol{\sigma}}|\, [\delta(\mathbf{x}_{12} - \boldsymbol{\sigma})\hat{b} - \delta(\mathbf{x}_{12} + \boldsymbol{\sigma})] \tag{2.2a}$$

with $\boldsymbol{\sigma} = \sigma\hat{\sigma}$, σ is the hard-sphere diameter, $\mathbf{V}_{12} = \mathbf{V}_1 - \mathbf{V}_2$, and $\hat{b}$ is an operator that changes velocities into postcollisional velocities,

$$\begin{aligned} \hat{b}\mathbf{V}_1 &= \mathbf{V}_1 - \hat{\boldsymbol{\sigma}}(\mathbf{V}_{12} \cdot \hat{\boldsymbol{\sigma}}) \\ \hat{b}\mathbf{V}_2 &= \mathbf{V}_2 + \hat{\boldsymbol{\sigma}}(\mathbf{V}_{12} \cdot \hat{\boldsymbol{\sigma}}) \end{aligned} \tag{2.2b}$$

The VACF is given in terms of C_s by

$$\begin{aligned} C_{\alpha\alpha'}(t) &\equiv \int d1\, d1'\, V_{1\alpha} V_{1\alpha'}' C_s(1t; 1') \\ &= \left\langle \sum_{i=1}^{N} v_{i\alpha}(t)\, v_{i\alpha'} \right\rangle \end{aligned} \tag{2.3a}$$

For the hard-sphere fcc crystal phase $C_{\alpha\alpha'}$ is diagonal in the vector labels α and α'. Below I show that the VACF is coupled to the spatially dependent correlation functions

$$C_{\alpha\alpha'}(\mathbf{x}_1, t) \equiv \int d\mathbf{V}_1\, d1'\, V_{1\alpha} V'_{1\alpha'} C_s(1t; 1')$$

$$= \left\langle \sum_{i=1}^{N} \delta[\mathbf{x}_1 - \mathbf{r}_i(t)]\, v_{i\alpha}(t)\, v_{i\alpha'} \right\rangle \tag{2.3b}$$

and

$$P_{\alpha'}(\mathbf{x}_1, t) \equiv \int d\mathbf{V}_1\, d1'\, V'_{1\alpha} C_s(1t; 1')$$

$$= \left\langle \sum_{i=1}^{N} \delta[\mathbf{x}_1 - \mathbf{r}_i(t)]\, v_{i\alpha'} \right\rangle \tag{2.3c}$$

Finally, because the variable 1′ in Eq. (2.1a) is not acted on by the kinetic operators and because we are interested in the correlation functions given by Eqs. (2.3), it is convenient to multiply Eq. (2.1a) by $V'_{1\alpha'}$ and integrate over 1′ to obtain an identical kinetic equation for

$$C_{s\alpha'}(1t) \equiv \int d1'\, V'_{1\alpha'} C_s(1t; 1')$$

$$= \left\langle \sum_{i=1}^{N} \delta[\mathbf{x}_1 - \mathbf{r}_i(t)]\, \delta[\mathbf{V}_1 - \mathbf{v}_i(t)]\, v_{i\alpha'} \right\rangle \tag{2.4}$$

From equilibrium statistical mechanics it follows that the initial values of the correlation functions defined by Eqs. (2.3) and (2.4) are given by

$$C_{\alpha\alpha'}(t=0) = \frac{Vn_0}{\beta_0 m}\, \delta_{\alpha\alpha'} \tag{2.5a}$$

and

$$C_{\alpha\alpha'}(\mathbf{x}_1, t=0) = \frac{n_{\text{eq}}(\mathbf{x}_1)}{\beta_0 m}\, \delta_{\alpha\alpha'} \tag{2.5b}$$

and

$$P_{\alpha'}(\mathbf{x}_1, t=0) = 0 \tag{2.5c}$$

and

$$C_{s\alpha'}(1, t=0) = n_{\text{eq}}(\mathbf{x}_1)\, \phi_{\text{eq}}(V_1)\, V_{1\alpha'} \tag{2.5d}$$

Here V is the system volume (the bulk limit is always implied), n_0 is the spatially averaged solid state number density, $\beta_0^{-1} = k_B T_0$ is the inverse equilibrium temperature, and m is the particle mass.

2.2. Moment Solution and Formal Equation of Motion

A standard way to solve kinetic equations (see, e.g., ref. 10) is to expand the distribution function, here $C_{s\alpha'}$, in terms of a complete set of polynomial functions of velocity, with coefficients that depend on space and time. With this and the kinetic equation, one can derive an infinite set of coupled space- and time-dependent differential equations for these coefficients. Usually one truncates the set of equations at some order n by setting all but the first n coefficients equal to zero. In the liquid state the interesting self-correlation functions, i.e., the self-density correlation function and the VACF, can be quantitatively computed for wavenumbers less than the inverse mean free path by using only two moments.(11) There is no reason that this aspect of solving Eq. (2.1a) should not also be valid in the solid state. Accordingly, we write

$$C_{s\alpha'}(1t) = \{P_{\alpha'}(\mathbf{x}_1, t) + \beta_0 m V_{1\alpha} C_{\alpha\alpha'}(\mathbf{x}_1, t)\}\, \phi_{\text{eq}}(V_1) \tag{2.6}$$

where the factors have been chosen such that Eqs. (2.3), (2.4), and (2.6) are consistent. The validity of this low-order moment solution will be discussed further in Section 3. Inserting Eq. (2.6) into the kinetic equation for $C_{s\alpha'}(1t)$ and integrating over $\mathbf{V}_1$ after multiplying by 1 and $V_{1\alpha}$ leads to two coupled equations for $P_{\alpha'}$ and $C_{\alpha\alpha'}$ that are given by

$$\partial_t P_{\alpha'}(\mathbf{x}_1, t) + \frac{\partial}{\partial x_{1\alpha}} C_{\alpha\alpha'}(\mathbf{x}_1, t) = 0 \tag{2.7a}$$

and

$$\begin{aligned}\partial_t C_{\alpha\alpha'}(\mathbf{x}_1, t) &+ \frac{n_{\text{eq}}(\mathbf{x}_1)}{\beta_0 m} \frac{\partial}{\partial x_{1\alpha}} \frac{P_{\alpha'}(\mathbf{x}_1, t)}{n_{\text{eq}}(\mathbf{x}_1)} \\ &+ \frac{2\sigma^2}{(\pi\beta_0 m)^{1/2}} \int d\hat{\boldsymbol{\sigma}}\, \hat{\sigma}_\alpha \hat{\sigma}_\gamma n_{\text{eq}}(\mathbf{x}_1 - \boldsymbol{\sigma})\, G_2[\mathbf{x}_1, \mathbf{x}_2 - \boldsymbol{\sigma} \,|\, n_{\text{eq}}]\, C_{\gamma\alpha'}(\mathbf{x}_1, t) = 0\end{aligned} \tag{2.7b}$$

Equation (2.7a) is just the exact conservation law for self-density fluctuations and Eq. (2.7b) is a relaxational-like equation for $C_{\alpha\alpha'}$. To obtain a single equation for $C_{\alpha\alpha'}(\mathbf{x}_1, t)$ from which the VACF can be obtained by integrating, or averaging, over space [cf. Eqs. (2.3)], we use Laplace transform techniques. For an arbitrary function $f(t)$, we define the Laplace transform by

$$f(z) = \int_0^\infty dt\, e^{-zt} f(t) \tag{2.8}$$

Equations (2.7) and the initial conditions given by Eqs. (2.5) yield the closed equation

$$\begin{aligned} &z^2 C_{\alpha\alpha'}(\mathbf{x}_1, z) - \frac{n_{\mathrm{eq}}(\mathbf{x}_1)}{\beta_0 m} \frac{\partial}{\partial x_{1\alpha}} \frac{1}{n_{\mathrm{eq}}(\mathbf{x}_1)} \frac{\partial}{\partial x_{1\gamma}} C_{\gamma\alpha'}(\mathbf{x}_1, z) \\ &\quad + \frac{2\sigma^2 z}{(\pi\beta_0 m)^{1/2}} \int d\hat{\boldsymbol{\sigma}}\, \hat{\sigma}_\alpha \hat{\sigma}_\gamma n_{\mathrm{eq}}(\mathbf{x}_1 - \boldsymbol{\sigma})\, G_2[\mathbf{x}_1, \mathbf{x}_2 - \boldsymbol{\sigma} \mid n_{\mathrm{eq}}]\, C_{\gamma\alpha'}(\mathbf{x}_1, z) \\ &= \frac{z n_{\mathrm{eq}}(\mathbf{x}_1)}{\beta_0 m} \delta_{\alpha\alpha'} \end{aligned} \tag{2.9}$$

If we define the normalized VACF by

$$\bar{C}_{\alpha\alpha'}(t) \equiv \frac{\beta_0 m}{V n_0} C_{\alpha\alpha'}(t) = \frac{\beta_0 m}{n_0 V} \int d\mathbf{x}_1\, C_{\alpha\alpha'}(\mathbf{x}_1, t) \tag{2.10a}$$

then Eq. (2.9) gives

$$\begin{aligned} &z^2 \bar{C}_{\alpha\alpha'}(z) - \frac{1}{n_0 V} \int d\mathbf{x}_1\, C_{\gamma\alpha'}(\mathbf{x}_1, z) \frac{\partial^2 \log n_{\mathrm{eq}}(\mathbf{x}_1)}{\partial x_{1\alpha}\, \partial x_{1\gamma}} + \frac{2\sigma^2 z}{n_0} \left(\frac{\beta_0 m}{\pi}\right)^{1/2} \\ &\quad \times \frac{1}{V} \int d\mathbf{x}_1\, d\hat{\boldsymbol{\sigma}}\, \hat{\sigma}_\alpha \hat{\sigma}_\gamma C_{\gamma\alpha'}(\mathbf{x}_1, z)\, n_{\mathrm{eq}}(\mathbf{x}_1 - \boldsymbol{\sigma})\, G_2[\mathbf{x}_1, \mathbf{x}_2 - \boldsymbol{\sigma} \mid n_{\mathrm{eq}}] \\ &= z\delta_{\alpha\alpha'} \end{aligned} \tag{2.10b}$$

Equation (2.10b) indicates that in the solid state $\bar{C}_{\alpha\alpha'}$ is coupled to the inhomogeneous correlation function $C_{\gamma\alpha'}(\mathbf{x}_1, z)$ due to the broken translational symmetry.

2.3. Approximate Solution

The simplest reasonable approximation to solve Eq. (2.9) is to assume

$$C_{\alpha\alpha'}(\mathbf{x}_1, t) = \frac{n_{\mathrm{eq}}(\mathbf{x}_1)}{\beta_0 m} \bar{C}_{\alpha\alpha'}(t) \tag{2.11}$$

i.e., the spatial and velocity degrees of freedom in Eq. (2.3b) decouple. Equation (2.11) can be easily shown to be exact at short times. In addition, it is shown below that Eq. (2.11) also leads to a long-time result that is consistent with current equilibrium theories of the solid state (see ref. 12 for a recent review). A more detailed discussion on the validity of Eq. (2.11) and corrections to it will be given below and in Section 3. Also note that Eq. (2.11) is equivalent to assuming that the time dependence of $P_{\alpha'}(\mathbf{x}_1, t)$

is given by $n_{\mathrm{eq}}(\mathbf{x}_1)$ at a time-dependent displaced position. This physically correct notion can be seen by using Eq. (2.11) in Eq. (2.7a).

Inserting Eq. (2.11) into Eq. (2.10b) leads to a damped oscillator equation for $\bar{C}_{\alpha\alpha'}(z)$,

$$[z^2+\omega_0^2+z/\tau]\,\bar{C}_{\alpha\alpha'}(z)=z\delta_{\alpha\alpha'} \tag{2.12a}$$

with the frequency ω_0 given by

$$\omega_0^2\delta_{\alpha\gamma}=\frac{1}{\beta_0 m n_0 V}\int d\mathbf{x}_1\,\frac{\partial n_{\mathrm{eq}}(\mathbf{x}_1)}{\partial x_{1\alpha}}\,\frac{\partial \log n_{\mathrm{eq}}(\mathbf{x}_1)}{\partial x_{1\gamma}} \tag{2.12b}$$

and the relaxation time τ is given by

$$\tau^{-1}\delta_{\alpha\gamma}=\frac{2\sigma^2}{n_0(\beta_0 m\pi)^{1/2}}\frac{1}{V}\int d\mathbf{x}_1\,d\hat{\boldsymbol{\sigma}}\,\hat{\sigma}_\alpha\hat{\sigma}_\gamma n_{\mathrm{eq}}(\mathbf{x}_1)\,n_{\mathrm{eq}}(\mathbf{x}_1-\boldsymbol{\sigma})\,G_2[\mathbf{x}_1,\mathbf{x}_2-\boldsymbol{\sigma}\,|\,n_{\mathrm{eq}}] \tag{2.12c}$$

Equations (2.12b) and (2.12c) are diagonal in the vector labels because of the cubic symmetry of a hard-sphere crystal. Equation (2.12a) is an equation one would write down phenomenologically for self-correlations in a harmonic system. In this sense, and in others,(13,14) the hard-sphere crystal is similar to a harmonic crystal. The crucial distinction we shall find is that the damping (or relaxation time τ) is very large (small). In dimensionless variables, the damping term in Eq. (2.12a) is of the same order as the spring constant term ($\sim\omega_0^2$).

The parameters given by Eqs. (2.12b) and (2.12c) can be easily related to known equilibrium functions. The relaxation time is given in terms of the solid state pressure p_s by(2)

$$\tau^{-1}=\frac{4F_1}{\sigma(\beta_0 m\pi)^{1/2}} \tag{2.13a}$$

with

$$F_1=\frac{p_s}{n_0 k_B T_0}-1 \tag{2.13b}$$

Equation (2.12b) for the frequency ω_0 can be related to the current density functional theories(12) of the solid state. These theories(12,15) parametrize $n_{\mathrm{eq}}(\mathbf{x}_1)$ by the spatially averaged density n_0, a lattice constant a, and a Gaussian width variable α,

$$n_{\mathrm{eq}}(\mathbf{x})=\frac{n_0}{\pi^{1/2}\alpha^{3/2}}\sum_{\mathbf{R}}\exp\left[\frac{-(\mathbf{x}-\mathbf{R})^2}{\alpha a^2}\right] \tag{2.14a}$$

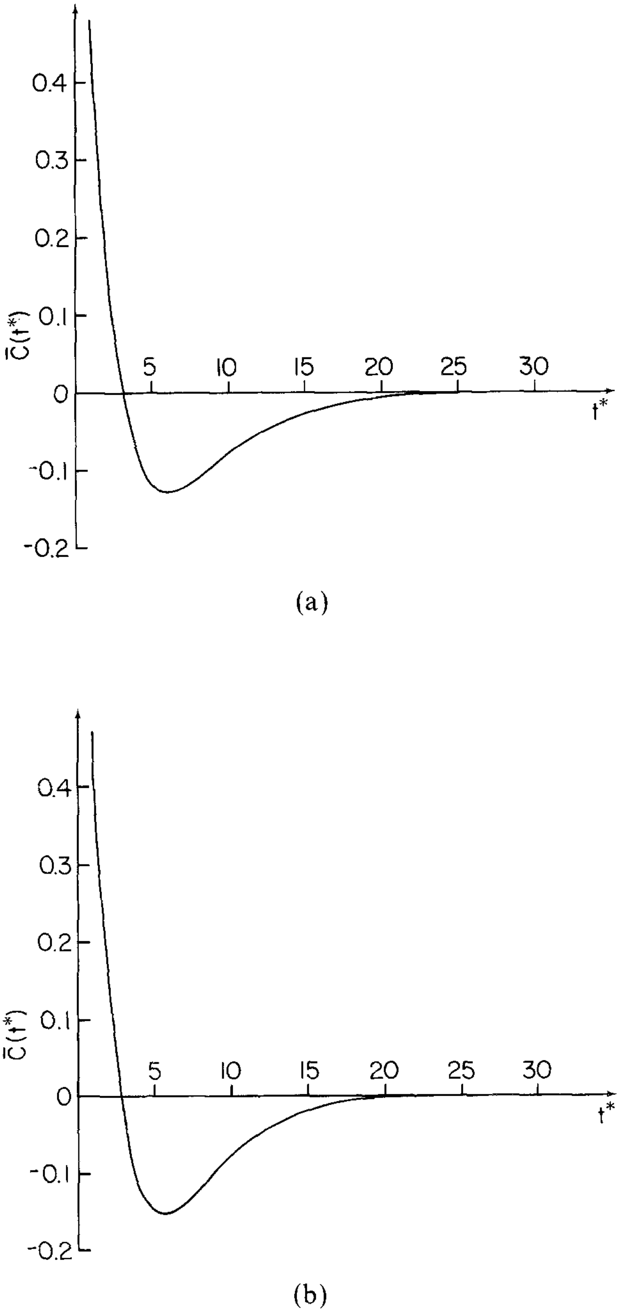
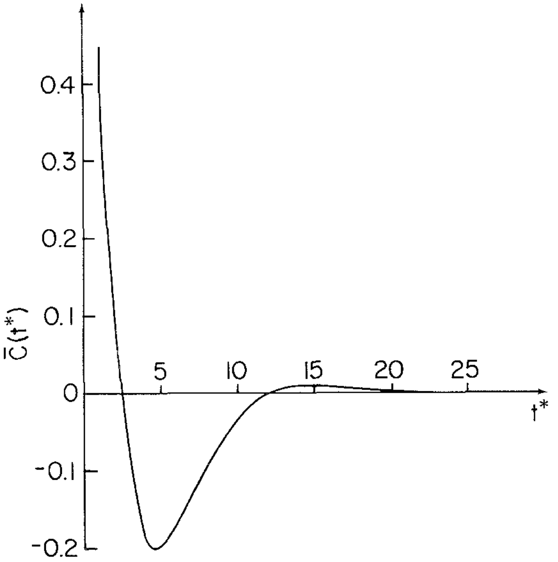


Fig. 1. VACF at a density (a) $n_0 = 0.7 n_{cp}$, (b) $n_0 = 0.736 n_{cp}$, and (c) $n_0 = 0.9 n_{cp}$.



(c)

Fig. 1 (*continued*)

Here **R** are the Bravais lattice vectors that generate an ideal fcc lattice. In practice, the Gaussian width variable is very small, which indicates that particles are extremely localized in a hard-sphere crystal. Also note that the parametrization of $n_{\text{eq}}(\mathbf{x})$ given by Eq. (2.14a) is in the spirit of an Einstein-oscillator approximation because there is only one frequency (related to α). This in turn is consistent with the simplicity of Eq. (2.12a). In the small-α limit, Eq. (2.12b) is easily evaluated with Eq. (2.14a) and one obtains

$$\omega_0^2 = \frac{2}{\beta_0 m \alpha a^2} \tag{2.14b}$$

Equation (2.12a) implies that the time integral of the VACF vanishes, which in turn implies zero self-diffusion coefficient in the solid state. This is clearly a general feature of Eqs. (2.9) and (2.10). If we define a dimensionless time by $t^* \equiv t/t_{\text{E}}$, with $t_{\text{E}} = \sigma(\beta_0 m\pi)^{1/2}/6F_1$ the Enskog collision time in the solid state, then in the time domain Eqs. (2.12)–(2.14) give

$$\begin{aligned}\bar{C}(t^*) \equiv \bar{C}_{xx}(t) = (1/2\Gamma)\{&(1+\Gamma)\exp[-(1+\Gamma)t^*/3] \\ &- (1-\Gamma)\exp[-(1-\Gamma)t^*/3]\}\end{aligned} \tag{2.15a}$$

with

$$\Gamma \equiv (1 - \pi\sigma^2/2F_1^2\alpha a^2)^{1/2} \tag{2.15b}$$

In principle, the VACF oscillates if Γ is imaginary and it is purely exponential if Γ is real. Note that the liquid state limit is $\alpha \to \infty$ or $\Gamma \to 1$, where Eq. (2.15a) reduces to the standard Enskog result, $\bar{C}(t^*) = \exp(-2t^*/3)$.

To determine if Γ is real or imaginary in general, we consider the hard-sphere crystal at three different densities. If n_{cp} is the crystal close-packed density, then the densities considered are $n_0 = 0.7n_{\text{cp}}$, $0.736n_{\text{cp}}$, and $0.9n_{\text{cp}}$. Physically they correspond to a metastable crystal, a crystal at its equilibrium coexistence density, and a crystal far from the solid-to-fluid transition density, respectively. For these states the parameters which determine Γ [Eq. (2.15b)] are taken from molecular dynamics experiments. From the hard-sphere pressure results(16) one obtains $F_1 = 9.0$, 10.223, and 28.69, respectively. From mean-squared displacement results(13) and Eq. (2.14a) one obtains $\langle R^2 \rangle/\sigma^2 = (3\alpha/2)(a/\sigma)^2 = 0.0312$, 0.0186, and 0.0015, respectively. These numbers and Eq. (2.15b) yield $\Gamma = 0.26$, $0.461i$, and $0.953i$, respectively. This indicates that in the entire equilibrium crystal phase the VACF is oscillatory. For these densities the VACF is graphed in Fig. 1. In practice we see that theory predicts that the oscillations near coexistence will be difficult if not impossible to detect (by the time they occur the VACF has decayed almost to zero) and that at higher densities they will be barely detectable.

Finally, we note that the consistency of Eqs. (2.11) and (2.14) can be checked dynamically by using Eqs. (2.15) to compute the mean-squared displacement. Using

$$C_{\alpha\alpha}(|t_1 - t_2|) = \left\langle \sum_{i=1}^{N} \mathbf{v}_i(t_1) \cdot \mathbf{v}_i(t_2) \right\rangle \tag{2.16a}$$

and integrating over t_1 and t_2 between zero and t and then letting $t \to \infty$, one obtains

$$2\bar{N}\langle \mathbf{R}^2 \rangle = \lim_{t \to \infty} \left\langle \sum_{i=1}^{N} [\mathbf{r}_i(t) - \mathbf{r}_i]^2 \right\rangle = 3\alpha a^2 \bar{N} \tag{2.16b}$$

where $\bar{N}$ is the average number of particles. Equation (2.16b) is consistent with Eq. (2.14a) and it indicates that Eq. (2.11) is not only exact for short times, but that it is also dynamically consistent for long times. This connection is possible because of the small-α approximation used in obtaining Eq. (2.14b). This suggests that Eq. (2.11) might become exact as $\alpha \to 0$.

3. DISCUSSION

I conclude with a number of remarks.

1. As far as I am aware, there are no published molecular dynamics (MD) data for the VACF in a hard-sphere crystal.[2] For a very dense, essentially glassy, hard-sphere system S. Brawer (unpublished results) has used MD to compute the VACF. For technical reasons (to avoid possible crystallization), he actually considered a two-component hard-sphere system. However, the fraction of the minority component was very small. Even at an effective reduced density of $n_0\sigma^3 \simeq 1.10$ (hard-sphere crystal–fluid coexistence is at $n_0\sigma^3 \simeq 1.04$) he observed no oscillations in the VACF. In fact, his results were very similar to the theoretical VACF shown in Fig. 1b. This is probably reasonable. On computer time scales one does not expect a large difference between the VACF in a glass and in a crystal. Brawer's results therefore support the idea that in hard-sphere systems the oscillations in the VACF are very small.

2. Some caveats are in order. First, Eq. (2.1a) is only an approximate kinetic equation. It completely neglects velocity correlation effects which are always present in dynamical quantities.[3] It does, however, exactly treat the static correlation effects that lead to the solid state.$^{(2)}$ In principle, an RET description will always lead to exact results for equilibriumlike quantities such as spring constants and elastic coefficients and to approximate results for damping rates and transport coefficients. The assumption used in this paper is that even in the solid state, the RET is a reasonable first approximation theory. The general problem of fluctuation (or velocity correlation) effects in the solid state remains to be investigated. It is possible that recollision effects neglected in Eq. (2.1a) could lead to a reduced (effective) damping rate in a generalized Eq. (2.12a). The oscillations in the VACF would then be more pronounced. To investigate fluctuation effects in the solid state it is probably simplest to use phenomenological ideas as in, for example, ref. 18. In this context, the RET results are interpreted as the bare theory results.

Second, even given Eq. (2.1a) as the starting kinetic equation, several approximations have been made in obtaining Eq. (2.12a). First, a low-moment solution method has been used [cf. Eq. (2.6)]. I have tried to improve upon Eq. (2.6) by including self-temperature (or energy) fluctuations ($\sim V_1^2$) as well as self-density and self-momentum density fluctuations. Again using Eq. (2.11), the generalization of Eq. (2.12a) turns out to be a cubic equation in the Laplace transform variable z. For all densities, the

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[2] I thank J. J. Erpenbeck and B. J. Adler for discussions on this point.

[3] The classic example is the long time tail effect.$^{(17)}$

cubic equation has one real root and two complex conjugate roots. This indicates that in principle the VACF oscillates at all the densities considered in Section 2. However, evaluation of $\bar{C}(t^*)$ within this approximation leads to curves which are essentially identical to those in Fig. 1 that were obtained using Eq. (2.6). I conclude that the results of the two-moment solution are stable in the sense that including additional moments does not appreciably modify the results.

A more serious approximation, given Eq. (2.1a), appears to be Eq. (2.11). Some discussion on this point was already given in Section 2.3. Additional insight can be gained by using the fact that Eq. (2.9) implies that $C_{\alpha\alpha}(\mathbf{x}_1, z)$ must have the periodicity of the underlying lattice. If Eq. (2.11) is generalized to

$$C_{\alpha\alpha'}(\mathbf{x}_1, t) = \frac{n_{\mathrm{eq}}(\mathbf{x}_1)}{\beta_0 m} \psi_{\alpha\alpha'}(\mathbf{x}_1, t) \tag{3.1a}$$

then the unknown function $\psi_{\alpha\alpha'}$ can be expanded in reciprocal lattice vectors $\mathbf{G}$ of the equilibrium lattice,

$$\psi_{\alpha\alpha'}(\mathbf{x}_1, t) = \sum_{\mathbf{G}} \mu_{\alpha\alpha'}(\mathbf{G}, t) \exp[i\mathbf{G} \cdot \mathbf{x}_1] \tag{3.1b}$$

If we also represent $n_{\mathrm{eq}}(\mathbf{x})$ in terms of reciprocal lattice vectors

$$n_{\mathrm{eq}}(\mathbf{x}_1) = n_0 \sum_{\mathbf{G}} \Phi_{\mathbf{G}} \exp[i\mathbf{G} \cdot \mathbf{x}_1] \tag{3.1c}$$

then the VACF is

$$\bar{C}_{\alpha\alpha'}(t) = \sum_{\mathbf{G}} \Phi_{-\mathbf{G}} \mu_{\alpha\alpha'}(\mathbf{G}, t) \tag{3.1d}$$

with $\Phi_{\mathbf{G}} = \exp[-G^2 \alpha a^2/4]$ from Eq. (2.14a). Inserting Eq. (3.1b) into Eq. (2.9) leads to coupled Bloch-like(3) equations for the expansion coefficients $\mu_{\alpha\alpha'}(\mathbf{G}, z)$. Note that, for an extremely well-ordered solid like a hard-sphere crystal an expansion in terms of a few reciprocal lattice vectors is not correct. From these coupled equations the following can be concluded. If the Fourier components with $G^2 \alpha a^2 > 1$ are neglected, then in the $\alpha \to 0$ limit the equation for the VACF reduces to Eq. (2.12a). This is in accord with the discussion at the end of Section 2.3. We next examine some of the possible consequences of the neglected Fourier components. First, they are exponentially damped in Eq. (3.1d) due to the $\Phi_{\mathbf{G}}$ factor. Second, the moment expansion leading to Eq. (2.1a) becomes problematic for large wavenumbers.(11) There is no physical reason to focus on a few low-order moments when the length scales become smaller than $a\alpha^{1/2}$. In terms of liquid-state ideas, this scale is essentially a mean free path distance between hard-sphere collisions. I conclude that the calculation given in Section 2 is at least consistent.

3. The mathematical cause of the negative part of the VACF in the solid state is the spring constant term $(\sim\omega_0^2)$ in Eq. (2.12a), or equivalently, the second term on the left-hand side of Eq. (2.7b), with $n_{\text{eq}}(\mathbf{x})$ spatially dependent. It is interesting to note that in (dense) liquid-state physics a reinterpreted Eq. (2.7b) also leads(18) to the negative part of the VACF. The main idea is to interpret Eq. (2.7b) as a fluctuating equation for the self-momentum density and $n_{\text{eq}}(\mathbf{x}) \to n(\mathbf{x}, t)$ as a fluctuating (in space and time) fluid number density.[4] Because $n(\mathbf{x}, t)$ decays slowly on the Enskog time scale, there is a restricted range of times where the fluid and solid state are very similar as far as the VACF is concerned.[5] A general point here is that effects that are due to fluctuations in the liquid state become more trivial average effects in the solid state.

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[4] To see the precise connection with ref. 18, in Eq. (2.7b) use the solid state condition(2)

$$\partial \log n_{\text{eq}}(\mathbf{x}_1)/\partial \mathbf{x}_{1\alpha} = \int d\mathbf{x}_2\, n_{\text{eq}}(\mathbf{x}_2)\, \partial C_2[\mathbf{x}_1, \mathbf{x}_2 \mid n_{\text{eq}}]/\partial x_{1\alpha}$$

Here C_2 is the solid-state two-particle direct correlation function.

[5] This argument is not valid for moderately dense hard-sphere gases because of large, positive, long-time tail effects.(17) As the density increases, these positive long-time tail effects become smaller and are masked for intermediate times(18) by a larger negative contribution to the VACF that is similar to the solid-state contribution discussed here. For $t \to \infty$ the positive long-time tail dominates and the VACF approaches zero from above in the fluid state.

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