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# Correlations for dilute hard core suspensions

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The generalized Smoluchowski equation is solved exactly for two particles interacting via a hard core potential in one, two, and three dimensions without the hydrodynamic interaction. From this solution coherent and incoherent intermediate scattering functions, memory functions, and transport coefficients are calculated. While many results relating to mutual diffusion are known, new results relating to self-diffusion are presented. These are compared with other exact and approximate results. The "hydrodynamic regime" for dynamic light scattering is discussed.

## I. INTRODUCTION

The generalized Smoluchowski (GSE) or Kirkwood-Riseman equation has proved to be a useful starting point for the description of polymers in solution,<sup>1,2</sup> and more recently, interacting colloidal particle suspensions.<sup>3</sup> In the latter case, the GSE has been used primarily to calculate properties of the incoherent and coherent intermediate scattering functions, which are measured by dynamic light scattering<sup>4</sup> or neutron spin-echo techniques.<sup>5</sup> Use of the GSE for these systems assumes that the diffusing particles are sufficiently large compared to bi-ions and counter-ions, so that the ion fluctuations are fully relaxed relative to the particles on the time scale of the experimental measurement. Thus, the ions serve only to produce an effective interaction between particles, and possibly, a contribution to the dilute particle solution diffusion constant. While arguments that include ion motion have been given<sup>6-8</sup> and use of the GSE for strongly interacting particles has been criticized,<sup>9,10</sup> many of the predicted relations agree with experimental data and this formulation remains a useful tool.

Cumulants which describe initial time decay of the intermediate scattering functions<sup>2,11</sup> have been derived from the GSE and from an equivalent Langevin equation method.<sup>12</sup> Projection operator techniques based on the GSE have given general expressions for the incoherent and coherent intermediate scattering functions in terms of memory functions.<sup>13,14</sup> Examination of the memory functions on large length scales [small scattered wave vector ( $\equiv k$ ) limit] indicates that the coherent intermediate scattering function decays exponentially in time.<sup>13</sup> This assumes that higher order spatial derivatives in the equation of motion for the scattering function can be neglected. The corresponding incoherent intermediate scattering function does not decay exponentially in time for small  $k$ . The self-diffusion described by the incoherent scattering function is initially free diffusion but is subsequently hindered by the presence of other particles. This produces a change in time scales for self-diffusion.

Hydrodynamic regime (large time-small  $k$ ) calculations of the coherent intermediate scattering function, using the GSE with a small time factorization approximation for the particle distribution functions, have produced exponential time decay rates identical to the small  $k$  limit of the first cumulant.<sup>3,15,16</sup> This is not

surprising because there is no expected time scale separation for this scattering function. The memory function tends to zero in this limit. Corresponding calculations for the incoherent intermediate scattering function<sup>17</sup> also give a first cumulant result, which is surprising because there should be a time scale separation between initial and large time decay for this function. The incoherent scattering memory function is not expected to be zero in general. Other calculations of the self-diffusion or incoherent scattering function have produced equally questionable results, which have been discussed recently in the literature.<sup>18</sup> Fluctuation dissipation theorems used to calculate self-friction factors and projection operator methods used for calculating self-diffusion constants may prove to be the most reliable method for studying self-diffusion in these systems.<sup>19,20</sup> However, results calculated from these methods have been based on certain approximations. For example, the self-diffusion constants for hard spheres and screened Coulomb interactions have been calculated from a *weak coupling* expression derived by projection operator methods.<sup>18</sup>

In this communication, the GSE is solved *exactly* for particles interacting via a hard core potential in one, two, and three dimensions without hydrodynamic interactions. From the exact solution, the coherent and incoherent scattering functions are found. Memory functions and diffusion constants are calculated. A discussion of previous approximate calculations of the "hydrodynamic regime" is given. It is hoped that these results will provide a rigorous check for many of the more approximate calculations.

## II. THEORETICAL CALCULATIONS

The GSE for two hard core particles in any dimension may be written as

$$\partial P / \partial t = D \nabla_1^2 P + D \nabla_2^2 P, \quad (2.1)$$

where the particle interactions will be handled by a boundary condition on  $P$ , where  $P$  is the probability (or Green's function) for finding the two particles at positions  $\vec{r}_1$  and  $\vec{r}_2$  at time  $t$ , given some initial positions  $\vec{r}_{10}$  and  $\vec{r}_{20}$  at  $t=0$ . The infinite dilution diffusion constant is given by  $D$ . Transforming to the center of mass system [ $R = (\vec{r}_1 + \vec{r}_2)/2$ ,  $\vec{r} = \vec{r}_1 - \vec{r}_2$ ], the GSE becomes

$$\partial P / \partial t = (D/2) \nabla_R^2 P + 2D \nabla_r^2 P. \quad (2.2)$$

The hard core interaction between two particles of dia-

meter  $\sigma$  is produced by requiring that

$$\partial P / \partial r = 0, \quad \text{when } r \rightarrow \sigma. \quad (2.3)$$

We also require that  $P$  be normalizable. The desired solution is found by considering  $P(\bar{R}, \bar{r}, t)$  to be a product of two solutions: (1) free diffusion of the center of mass  $V(\bar{R}, t)$ , and (2) restricted diffusion for the relative coordinates  $W(\bar{r}, t)$ . The solution to the free diffusion problem for  $V(\bar{R}, t)$  is well known<sup>21</sup> and will not be reproduced. The restricted diffusion problem for the relative coordinate with proper boundary conditions may be constructed and expressed in terms of the Laplace transformed time variable  $s$ .

We have found the solution for  $W(\bar{r}, s)$  in dimension  $d$  to be

$$W(r, r_0, s) = \frac{1}{2Dq} \exp(-qr_0) \{ \sinh(qr_0) + \exp[-q(r_0 - \sigma)] \cosh(q\sigma) \}, \quad (d=1), \quad (2.4)$$

$$W(\bar{r}, \bar{r}_0, s) = \frac{1}{2D} \sum_{m=0}^{\infty} \{ \exp[i m(\phi - \phi_0)] / 2\pi \} K_m(qr_0) \times \left[ I_m(qr_0) - K_m(qr_0) \frac{I'_m(q\sigma)}{K'_m(q\sigma)} \right], \quad (d=2), \quad (2.5)$$

$$F(k, t) = \frac{1}{2V_d^2} \sum_{i,j=1}^2 [\delta_s \delta_{ij} + \delta_d(1 - \delta_{ij})] \iint \exp[i\bar{k} \cdot (\bar{r}_i - \bar{r}_{j0})] P(\bar{r}_1, \bar{r}_2, \bar{r}_{10}, \bar{r}_{20}, t) \theta(\bar{r}_{10}, \bar{r}_{20}) d\bar{r}_{10} d\bar{r}_{20} d\bar{r}_1 d\bar{r}_2 \\ = \frac{1}{2V_d^2} \sum_{\pm} \int \exp[i\bar{k} \cdot (\bar{R} - \bar{R}_0)] V(\bar{R}, \bar{R}_0, t) dR_0 dR \int \{ \delta_s \exp[\pm i\bar{k} \cdot (\bar{r} - \bar{r}_0)/2] + \delta_d \exp[\pm i\bar{k} \cdot (\bar{r} + \bar{r}_0)/2] \} W(\bar{r}, \bar{r}_0, t) \theta(r_0) d\bar{r}_0 d\bar{r}, \quad (2.7)$$

where  $V_d$  is the sample volume size in dimension  $d$  and  $\theta(r_0)$  is a unit step function resulting from the equilibrium distribution of the two particles. For the incoherent scattering function, we set  $\delta_s = 1$  and  $\delta_d = 0$ . For the coherent scattering function, we set  $\delta_s = \delta_d = 1$ . For  $\delta_s = 0$  and  $\delta_d = 1$ , we have the distinct intermediate scattering function. The integrals over the center of mass and relative coordinates may be carried out separately. The center of mass integral, which represents free diffusion, produces the familiar exponential time decay, which is Gaussian in  $k$ , with a renormalized diffusion constant [i.e.,  $\exp(-Dk^2t/2)$ ]. The integrals over the relative coordinates may be carried out using the results in [Eqs. (2.4)–(2.6)] to produce the spatially transformed scattering functions  $W(k, t)$ . Unfortunately, the results in [Eqs. (2.4)–(2.6)] are in terms of the variable  $s$  and are difficult to invert. However, if we wish to express the result for the full coherent and incoherent scattering functions in terms of the variable  $s$ , the time exponential function from the center of mass coordinate simply produces a shift in the Laplace variable between the relative and full correlation functions. For example,

$$\tilde{F}(k, s) = \int_0^{\infty} \exp(-st) F(k, t) dt \\ = \int_0^{\infty} \exp(-st) \exp(-Dk^2t/2) W(k, t) dt \\ = \tilde{W}(k, s + Dk^2/2), \quad (d=1, 2, \dots). \quad (2.8)$$

$$W(\bar{r}, \bar{r}_0, s) = \frac{q}{2D} \sum_{l=0}^{\infty} \sum_{m=-l}^l Y_{lm}^*(\Omega) Y_{lm}(\Omega_0) \\ \times k_l(qr_0) \left[ i_l(qr_0) - k_l(qr_0) \frac{i'_l(q\sigma)}{k'_l(q\sigma)} \right], \quad (d=3). \quad (2.6)$$

The one-dimensional solution may be found by the method of images<sup>14</sup> and has been included for completeness. Here,  $I_m$  and  $K_m$  are modified Bessel functions of the first and second kind, while  $i_l$  and  $k_l$  are corresponding spherical Bessel functions;  $I'_m$ ,  $K'_m$ ,  $i'_l$ , and  $k'_l$  are derivatives of the functions with respect to  $\sigma$ ;  $r_0$  and  $r_c$  refer to the greater and lesser of the two quantities  $r$  and  $r_0$ , respectively;  $\phi$  and  $\phi_0$  are the angular directions of  $\bar{r}$  and  $\bar{r}_0$ , respectively;  $Y_{lm}(\Omega)$  and  $Y_{lm}(\Omega_0)$  are spherical harmonic functions of the angular directions of  $\bar{r}$  and  $\bar{r}_0$ , respectively; and  $q = \sqrt{s/2D}$ .

The coherent and incoherent intermediate scattering functions [ $F_c(k, t)$  and  $F_I(k, t)$ , respectively] are determined from  $P = WV$  as follows:

With this observation the following results are found for the intermediate scattering functions:

$$F(k, s) = [s + Dk^2]^{-1} \{ s(k) + \delta_d \delta_{k,0} + Dk^2 [s + Dk^2]^{-1} [s(k) - \delta_s] - D[s + Dk^2]^{-1} \Sigma(k, u) \}, \quad (d=1, 2, \dots), \quad (2.9)$$

where

$$u = [s/2D + k^2/4]^{1/2} \sigma, \quad (2.10)$$

and  $\delta_{k,0}$  is a Kronecker delta function. We obtain

$$\Sigma(k, u) = c [\delta_s - \delta_d \cos(k\sigma)] (-k^2\sigma/u), \quad (d=1), \quad (2.11)$$

$$s(k) = \delta_s - \delta_d (2c \sin(k\sigma))/k, \quad (d=1), \quad (2.12)$$

$$\Sigma(k, u) = 4\pi\sigma c \sum_{m=0}^{\infty} [\delta_s + (-1)^m \delta_d] \times \left[ J'_m\left(\frac{k\sigma}{2}\right) \right]^2 \frac{K_m(u)}{K'_m(u)}, \quad (d=2), \quad (2.13)$$

$$s(k) = \delta_s - \delta_d [2\pi\sigma c J_1(k\sigma)]/k, \quad (d=2), \quad (2.14)$$

$$\Sigma(k, u) = 8\pi\sigma^2 c \sum_{l=0}^{\infty} (2l+1) [\delta_s + (-1)^l \delta_d] \times \left[ j'_l\left(\frac{k\sigma}{2}\right) \right]^2 \frac{k_l(u)}{k'_l(u)}, \quad (d=3), \quad (2.15)$$

$$s(k) = \delta_s - \delta_d [4\pi\sigma^2 c j_1(k\sigma)]/k, \quad (d=3). \quad (2.16)$$

Here, the  $J_m$  are Bessel functions; the  $j_l$  are spherical

Bessel functions;  $J'_m$  and  $j'_l$  are derivatives with respect to  $\sigma$ ;  $S(k)$  are static structure factors; and  $c$  is the concentration.

The initial values and cumulants for the scattering functions may be found from

$$F(k, t=0) = \lim_{s \rightarrow \infty} s \bar{F}(k, s). \quad (2.17)$$

Since  $\Sigma \rightarrow 1/\sqrt{s}$  as  $s \rightarrow \infty$ , we find

$$F(k, t=0) = S(k) + \delta_{k,0} \delta_d, \quad (d=1, 2, \dots). \quad (2.18)$$

The first cumulant is given by

$$\begin{aligned} K_1 &= \partial \ln F(k, t=0) / \partial t \\ &= [1/F(k, 0)] \lim_{s \rightarrow \infty} [s \bar{F}(k, s) - F(k, 0)] \\ &= -Dk^2 (\delta_s + \delta_{k,0} \delta_d) / [S(k) + \delta_{k,0} \delta_d] \\ &= -Dk^2 / S(k), \quad \text{for } k \neq 0, \quad \delta_s = 1, \quad (d=1, 2, \dots). \end{aligned} \quad (2.19)$$

Again,  $\Sigma$  does not contribute in the large  $s$  limit. The initial values and cumulants presented here satisfy general relationships<sup>11,12</sup> and serve as a check for the calculations. The second cumulants are found to be infinite for hard core suspensions, which indicates that a cumulant expansion in integer powers of  $t$  does not exist. An evaluation of general expressions<sup>11</sup> for the second cumulant will give the same result because the interaction potential is discontinuous.

Projection operator methods have been used to express the intermediate scattering functions in terms of memory functions<sup>13,14</sup>

$$\partial F(k, t) / \partial t = +K_1 F(k, t) + \int_0^t M(k, \tau) F(k, t-\tau) d\tau, \quad (2.20)$$

where  $K_1$  is the first cumulant and  $M$  is the memory function. Because we have expressions for the intermediate scattering functions, we can easily find formal expressions for the corresponding memory functions using the results presented in [Eqs. (2.9)–(2.19)]. To this end, we note that the Laplace time transform of the memory function is given by

$$\tilde{M}(k, s) = s - K_1 - \tilde{F}(k, 0) / \tilde{F}(k, s). \quad (2.21)$$

While general expressions for  $M$  may be found, we shall only present the small  $k$  limit. In this limit to order  $k^2$ , we find for the coherent memory function

$$\tilde{M}_C(k, s) = 0, \quad (d=1, 2, \dots). \quad (2.22)$$

In the same limit, the incoherent memory functions are found to be

$$\tilde{M}_I(k, s) = cDk^2 / \sqrt{\frac{s}{2D}}, \quad (d=1), \quad (2.23)$$

$$\begin{aligned} \tilde{M}_I(k, s) &= -\pi\sigma cDk^2 K_1 \left( \sqrt{\frac{s}{2D}} \sigma \right) / 2K_1' \left( \sqrt{\frac{s}{2D}} \sigma \right), \\ &\quad (d=2), \end{aligned} \quad (2.24)$$

$$\begin{aligned} \tilde{M}_I(k, s) &= -2\pi\sigma^2 cDk^2 k_1 \left( \sqrt{\frac{s}{2D}} \sigma \right) / 3k_1' \left( \sqrt{\frac{s}{2D}} \sigma \right), \\ &\quad (d=3). \end{aligned} \quad (2.25)$$

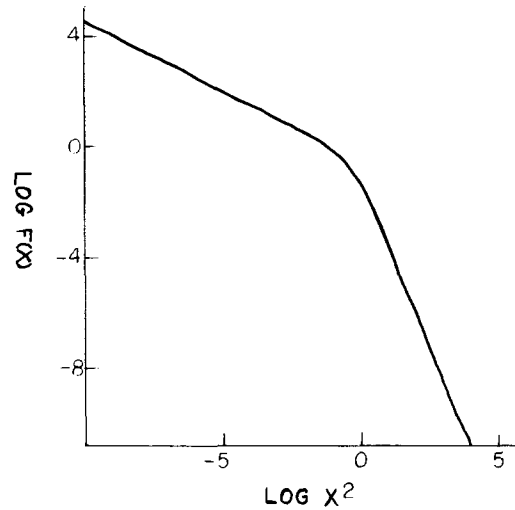


FIG. 1. The time dependent portion of the single particle force correlation function  $F(x)$  in three dimensions is given as a function of  $x^2 = (8Dt/\pi\sigma^2)$ . It should be noted that the initial slope is  $\frac{1}{2}$  and is reminiscent of the one-dimensional decay, while the long time slope is  $\frac{5}{2}$  and represents a quicker loss of correlation due to the greater spatial freedom in three dimensions.

The small  $k$  results for the coherent memory functions are proportional to total force correlation functions, and are zero because the total force at any given time is zero.<sup>13</sup> The small  $k$  results for the incoherent memory function are proportional to single particle force correlation functions and are not zero in general. The small  $k$  results for the incoherent memory function in one and three dimensions are inverted to make the time dependence explicit. For  $d=1$  we find<sup>14</sup>

$$M_I(k, t) = cDk^2 [2D/\pi t]^{1/2} + O(k^4), \quad (2.26)$$

and for  $d=3$  we find

$$M_I(k, t) = 8\pi\sigma cD^2 k^2 F(x)/3, \quad (2.27)$$

with

$$F(x) = \left\{ \frac{1}{x} \left[ \frac{1}{\pi} - xf(x) \right] \right\}, \quad (2.28)$$

where  $f(x)$  is an auxiliary Fresnel integral

$$f(x) = \left[ \frac{1}{2} - \text{Si}(x) \right] \cos\left(\frac{\pi x^2}{2}\right) - \left[ \frac{1}{2} - \text{Ci}(x) \right] \sin\left(\frac{\pi x^2}{2}\right), \quad (2.29)$$

and

$$x = (8Dt/\pi\sigma^2)^{1/2}. \quad (2.30)$$

Here,  $\text{Ci}(x)$  and  $\text{Si}(x)$  are the Fresnel cosine and sine integrals, respectively. The memory function for three dimensions is plotted in Fig. 1. It is seen that the effect of the hard sphere interaction is to produce an infinite zero time correlation which decays initially as  $t^{-1/2}$ , as in one dimension. For long times, it decays as  $t^{-5/2}$ . This change from a slow one-dimensional decay at small times to a more rapid decay at larger times reflects the greater freedom present in three dimensions. The corresponding calculation in two dimensions has not proven to be as tractable. It seems likely, however, that an initial decay of  $t^{-1/2}$  followed by a long time decay of  $t^{-d+1/2}$  is the general result.

Once we have the cumulants and the memory functions, it is possible to calculate the mutual and self-diffusion constants for these simple systems. These may also be determined from the intermediate scattering functions directly as they are generating functions for position or displacement moments. The diffusion constants are given by the following ordered limiting process:

$$D = -\lim_{s \rightarrow 0} \lim_{k \rightarrow 0} [K_1 + M] / k^2, \quad (2.31)$$

from which we find

$$D_c = D(1 + 2\phi), \quad (d=1), \quad (2.32)$$

$$D_I = -\infty, \quad (d=1), \quad (2.33)$$

$$D_c = D(1 + 4\phi), \quad (d=2), \quad (2.34)$$

$$D_I = D(1 - 2\phi), \quad (d=2), \quad (2.35)$$

$$D_c = D(1 + 8\phi), \quad (d=3), \quad (2.36)$$

$$D_I = D(1 - 2\phi), \quad (d=3), \quad (2.37)$$

where  $\phi$  is the  $d$ -dimensional volume fraction. The mutual diffusion coefficient  $D_c$  has the expected form which has been found before by different methods.<sup>22</sup> The self-diffusion constant  $D_I$  is a new result and indicates a behavior quite different from  $D_c$ . The self-diffusion coefficients are decreased from the  $D$  value due to the direct hard sphere interactions. In one dimension, the self-diffusion constant is not defined and the particle's mean square displacement does not grow linearly with time at large times. This is due to the fact that the hard core interaction restricts the allowed motions in one dimension.

### III. DISCUSSION

The results for the coherent intermediate scattering functions, the first cumulants, the low  $k$  limit of the memory functions and the diffusion constants are well-known and serve as a check of the calculation. The results for the incoherent intermediate scattering functions are new and have, until now, only been calculated approximately. In the absence of hydrodynamic interactions, the mutual diffusion constant  $D_c = \partial \pi / \partial c|_T / f_c$  shows a modification from the infinitely dilute value of  $D$ , due to thermodynamic forces  $\partial c / \partial \pi|_T = S(O)$ . There is no modification of the mutual friction factor  $f_c = f$  due to direct interactions. On the other hand, the self-diffusion constant  $D_I = kT / f_I$  shows no modification from the infinite dilution value of  $D$  due to thermodynamic forces. However, it exhibits a decreased diffusion rate due to the effect of direct interactions on increasing the self-friction factor  $f_I = f(1 + 2\phi)$ . The two friction factors  $f_I$  and  $f_c$  are certainly not the same for dilute hard sphere suspensions as anticipated by general arguments.<sup>13,23,24</sup> This effect on the self-diffusion constant and friction factor is contrary to some arguments,<sup>25,26</sup> but is consistent with fluctuation dissipation calculations of the friction factor,<sup>19,20</sup> projection operator based weak coupling calculations,<sup>18</sup> and mode coupling calculations of the self-diffusion constant.<sup>3</sup> This is also consistent with intuitive arguments which consider neighboring particles to "cage" and hinder the motion of a given particle.<sup>27</sup>

Explicit but approximate calculations for direct (three-dimensional) hard sphere interaction effects are in fair agreement with the exact result. Friction factor calculations<sup>20</sup> have given  $f_I = f(1 + 2.67\phi)$  [ $D_I = D(1 - 2.67\phi)$ ] while the weak coupling<sup>18</sup> and mode coupling<sup>3</sup> calculations give  $f_I = f(1 + 1.33\phi)$  [ $D_I = D(1 - 1.33\phi)$ ]. Other approximate calculations have included hydrodynamic interactions and may or may not include the direct interactions. Einstein's classic result<sup>28</sup> for the viscosity of a dilute solution of hard spheres does not include direct interactions and is often taken to imply  $f_I = f(1 + 2.5\phi)$ . Other hydrodynamic calculations<sup>29</sup> suggest larger increases in the friction factor from  $f_I = f(1 + 6.8\phi)$  to  $f(1 + 7.2\phi)$ :

As stated previously, projection operator techniques have been used to argue that there may be no time scale separation between the initial cumulant decay for small  $k$  and the hydrodynamic regime for the coherent intermediate scattering function. This result is also produced by purely hydrodynamic regime calculations and implies that for sufficiently small  $k$ , dynamic light scattering experiments should measure an exponential time decay which is Gaussian in  $k$ . However, these results hold only if the many particle system has a hydrodynamic regime, which means that spatial derivatives of order three or greater may be neglected in the equation of motion for the coherent intermediate scattering function. This may not be true for dilute suspensions. For example, consider the coherent intermediate scattering function for two harmonically coupled particles diffusing in one dimension. While this model is physically unrealistic, it is instructive, and the delayed Vineyard approximation<sup>30</sup> may be shown by systematic derivation to be an exact relation. For this system, we have<sup>16</sup>

$$\begin{aligned} F_c(k, t) = & \exp(-Dk^2\{t + [1 - \exp(-At)]/A\}/2) \\ & + \cos(ka) \exp(-Dk^2/A) \\ & \times \exp(-Dk^2\{t - [1 - \exp(-At)]/A\}/2), \end{aligned} \quad (3.1)$$

and

$$F_I(k, t) = \exp(-Dk^2\{t + [1 - \exp(-At)]/A\}/2), \quad (3.2)$$

where  $a$  is the equilibrium particle separation,  $\alpha$  is the coupling constant,  $\beta^{-1} = kT$ , and  $A = 8\alpha\beta D$ . These functional forms give the proper structure factors, cumulants, and memory functions. In addition, they demonstrate the fact that  $M_c = 0$  to order  $k^2$ . However, for large times, both intermediate scattering functions decay exponentially in time with decay rate  $Dk^2/2$ . Thus, both scattering functions show a change in time scale when the initial decay is compared to the long time decay. The coherent intermediate scattering function does not have a simple exponential time decay for all times. However, the intermediate scattering function presented in Eq. (3.1) may be written as a sum of exponential time decays. The amplitude of each of the exponentials depends on  $k$  and is a higher power of  $k$  for larger decay rates. Thus, in the low  $k$  limit, only the lowest exponential decay is evident as the amplitudes of all the others is exceedingly small.

Thus,  $F_c$  tends to a simple exponential decay and  $M_c$  tends to zero in the small  $k$  limit; *but the rate of decay of  $F_c$  in this limit is not given by the first cumulant for  $F_c$  in this model.* This happens because the system is not hydrodynamic and  $F_c$  requires higher order spatial derivatives for a proper description.

While the long time behavior of the hard core problems has not been analyzed in detail, it seems that a structure similar to the harmonic model may hold. The cumulants and diffusion constants depend on concentration, yet the pole and branch cut structure of the  $\bar{F}_c(k, s)$  and  $\bar{F}_l(k, s)$  functions in [Eqs. (2.9)–(2.16)] do not. Only the weighing of the various poles depends on concentration. Thus, it is difficult to see how  $F_c(k, t)$  might have a simple exponential time decay for all times at sufficiently small  $k$  with the proper concentration dependence for the decay rate. We conclude that care must still be exercised in interpreting the results of light scattering experiments for the measurement of transport coefficients.

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