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REVIEW ARTICLE

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Dynamics of the colloidal suspensions

Abstract This article offers a survey on our current knowledge of the dynamics of the colloidal suspension, where each particle experiences the friction force with solvent, hydrodynamic interaction, and potential force from surrounding particles and thermodynamic force. It further contains a summary of the basic concepts about microstructures and equilibrium properties, and of analytical and numerical methods, which are relevant for the theoretical description of the suspensions. The description of the dynamics of colloidal particles, based on the generalized Smoluchowski equation, is justified for the time scale accessible in DLS experiments. The combined influence of hard sphere or electrostatic potential and solvent-mediated hydrodynamic interaction on the short-time dynamics of monodisperse suspensions is investigated in detail. A thorough study of tracer-diffusion in hard sphere and charge-stabilized suspensions is presented. Mean-square displacements and long-time tracer-diffusion coefficients are calculated with two alternative approximations, i.e., a mode-coupling scheme and a single relaxation time ansatz.

Keywords colloidal suspension, hydrodynamic interaction

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1 Introduction

Colloidal suspensions are systems where small particles disperse in solvents, being categorized as a kind of the so-called “soft matters”. The size of colloidal particles normally ranges from several nanometers to micrometers, with the shape being spherical, cylindrical or others. It is obvious that the magnitude of colloidal particles is much larger than that of molecules, so that quantum effects do not play an important role. Meanwhile, since the particles are small enough to perform Brownian motion at room temperature, they do not sediment quickly under gravitation. Colloidal suspensions are nowadays widespread in human life, among which milk is the most popular one.

Colloidal systems have been studied for many years, however, the study for the diffusion velocities of many materials by Thomas Graham, an English scientist, in 1861, is regarded as the beginning of colloidal science. He not only introduced the concept of “colloid”, but also termed many colloidal systems, such as Sol and Gel, etc., which have become the everyday vocabulary of colloid chemists. The invention of microscopes at the beginning of the last century greatly promoted the development of colloidal science; and the improvement of experimental techniques in the following years further advanced the study of colloidal science, among which colloid chemistry has become an independent branch.

Colloidal suspensions are complex systems where many phases coexist, due to the fact that the particles can be of different shapes and sizes, while both the magnitude and the diversity of magnitudes can be varied in individual systems. This, accordingly, makes it a formidable task to do theoretical research quantitatively on the interactions between colloidal particles and the structures and properties of colloidal particles from the standpoint of physics. Furthermore, modern physics, characterized by quantum mechanics and relativity since the twentieth century, has attracted most of the attentions of theoretical physicists, resulting in few profound theoretical studies in colloid physics. However, study in colloid chemistry has been very fruitful and has contributed largely to the theoretical research in colloid physics. In the past 40 years, the production of nearly uniform spherical macromolecule colloidal particles has been made possible. The systematic studies on the fine fabricated model colloid systems, both experimentally and theoretically, deepen greatly the understanding of the interaction, structure and dynamics of colloids. The colloidal particles can be in the gas, liquid and solid state. By changing the condition of fabrication or by

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reprocessing one can fine-tune the interactions of colloid particles and obtain more structures and rich symmetries that may be hard to attain in ordinary solids.

Each particle in colloidal suspensions experiences friction force with the solvent, hydrodynamic interaction, and potential force from adjacent particles and thermodynamic force. The main topic in colloidal dynamics is just to investigate the motion of colloidal particles under all these forces. Therefore, this paper presents a thorough description of analytical and numerical methods used in studying the suspensions of spherical colloids. We give out the detailed mathematical derivation, as well as explicit physical interpretation to some of the important phenomena.

2 Time scales and transport equations

The dynamics of colloidal systems depends greatly on the time scales under which they are explored. Therefore, we first make some qualitative analysis [1, 2, 3, 4].

Since the size of colloidal particles is much larger than that of the solvent molecules, which implies that when the relatively larger (thus slower) colloidal particles are in non-equilibrium configuration, the solvent has quickly reached the equilibrium distribution, with the relaxation time 10^{-13}–10^{-12}s. Hence it is reasonable to regard the solvent as continuum fluid medium, which experiences longitudinal and transverse collective excitations, on the time scale of dynamics of colloidal particles. The longitudinal excitation of fluid velocity corresponds to compressive sound wave. If the radius of a colloidal particle is denoted by a, while sound velocity by υ_s, the time taken for the sound wave to propagate a distance a, i.e., $\tau_s = a/\upsilon_s$, is another characteristic time. When the particle radius is 10–100 nm, τ_s is approximately 10^{-12}–10^{-11}s. On the time scale much larger than τ_s, the sound wave is regarded to propagate at infinite speed, where the motion of the solvent can be described by Navier-Stokes equation for incompressible fluids [5]:

$$\rho_s\left[\frac{\partial \boldsymbol{u}}{\partial t}+(\boldsymbol{u}\cdot\nabla)\boldsymbol{u}\right]=-\nabla p+\eta\Delta\boldsymbol{u} \tag{2.1}$$

$$\nabla\cdot\boldsymbol{u}=0 \tag{2.2}$$

The fluid on the surfaces of colloidal particles satisfies stick boundary condition, i.e., there is no relative slip between colloidal particles and fluid [2]. Here $p(\boldsymbol{r},t)$ is the pressure, ρ_s the mass density of the solvent, and η the shear viscosity of the solvent. The Reynolds number for a typical colloidal suspension is $Re \ll 1$, e.g., in water, a=100 nm, $\eta = 0.01\,g/(\mathrm{cm}\cdot\mathrm{s})$ and $\upsilon = 0.1\mathrm{cm/s}$ yield $Re = \rho\upsilon a/\eta = 10^{-4}$ .In this sense, the nonlinear inertial term in Eq. (2.1) can be ignored. By taking curl of Eq. (2.1), we obtain

$$\frac{\partial}{\partial t}(\nabla\times\boldsymbol{u})=\frac{\eta}{\rho_s}\Delta(\nabla\times\boldsymbol{u}) \tag{2.3}$$

which is simply the diffusion equation of vorticity $\nabla\times\boldsymbol{u}$, with η/ρ_s the diffusion coefficient of the vorticity. It can easily be evaluated that the time taken for the vorticity to diffuse a distance a, i.e., the viscosity relaxation time, $\tau_\eta = \rho_s a^2/\eta$, is between 5×10^{-10} and 10^{-8}s. On the time scale $t \gg \tau_\eta$,the transverse excitation of the solvent is also instantaneous, the motion of which can be described by the stationary linear Navier-Stokes equation for incompressible fluids, in addition to the stick boundary condition. Under such approximation, the picture of the interaction between colloidal particles and solvent is as follows: the diffusion motion of colloidal particles produces a velocity field, which on the time scale $t \gg \tau_\eta$ propagates instantaneously to influence the motion of other particles. This dynamic interaction is, however, just the hydrodynamic interaction. When considering the motion on the time scale $t \gg \tau_\eta$, the observed velocity of colloidal particles is actually the diffusion velocity, rather than the instantaneous velocity. When an individual colloidal particle experiences the force $\boldsymbol{F}$, its diffusion velocity should be $\upsilon = \xi_0^{-1}\boldsymbol{F}$, where $\xi_0 = 6\pi\eta a$ is the Stokes drag coefficient. The diffusion constant of an isolated particle, D_0, satisfies Einstein relation $D_0 = k_\mathrm{B}T/\xi_0$, yielding $\upsilon = (k_\mathrm{B}T)^{-1}D_0\boldsymbol{F}$. However, for a many-particle system where hydrodynamic interaction (hereafter we refer to as HI) is taken into account, the diffusion velocity of particle i, υ_i , depends on forces acted on particle i, as well as the forces acted on other particles, leading to [6]

$$\boldsymbol{\upsilon}_i = (k_\mathrm{B}T)^{-1}\sum_{j=1}^{N}\boldsymbol{D}_{ij}(\boldsymbol{r}^N)\cdot\boldsymbol{F}_j \tag{2.4}$$

where $\boldsymbol{D}_{ij}(\boldsymbol{r}^N)$ is translational diffusion tensor, relating the translational diffusion velocity to the force acted on the particle, which depends on the sizes of all particles in the suspension and the configuration $\boldsymbol{r}^N \equiv (\boldsymbol{r}_1,\boldsymbol{r}_2,\cdots,\boldsymbol{r}_N)$. From the above analysis that on time scale $t \gg \tau_\eta$, when hydrodynamic interaction can be regarded as instantaneously propagating, the relation between υ_i and $\boldsymbol{F}_j$ is linear. When $t \approx \tau_\eta$, there exists a retardation effect for HI; meanwhile, the particle velocity observed on this time scale is much larger than diffusion velocity, and therefore the solvent motion cannot be precisely described by linearized N-S equation, where linearity is no longer valid. However, in this paper we do not consider this complicated situation. In general the colloidal particles experience both translational and rotational motion, hence we should deal with these two motions simultaneously. For simplicity,we only discuss the translational motion of colloidal particles here, similar to which the rotational motion can be studied, e.g., the rotational diffusion tensor may in parallel be defined [7].

We have so far considered the characteristic time related to the dynamics of the solvent on the basis of the size of colloidal particles. Now we start to discuss the characteristic time related to the motion of colloidal particles. The motion of an isolated colloidal particle with mass m in boundless fluid satisfies the phenomenological Langevin equation

$$m\dot{\upsilon} = \boldsymbol{F}^H(t) + \boldsymbol{R}(t) \qquad (2.5)$$

where $\boldsymbol{F}^H$ is the friction force acted on the colloidal particle by the solvent. $R(t)$ is the stochastic force originated from the fluctuation of solvent molecules, with the average 0, and normally assumed to be Gaussian distributed. Supposing that $\boldsymbol{F}^H = -\xi_0 \upsilon$, we obtain that the average value of the solution for Eq. (2.5), $\upsilon(t)$, is $\langle \upsilon(t) \rangle = \upsilon(0)\,\mathrm{e}^{-t\xi_0/m} = \upsilon(0)\,\mathrm{e}^{-t/\tau_B}$. This, however, means that the characteristic time for the velocities of colloidal particles approaches equilibrium $\tau_B = m/\xi_0$, i.e., Brownian relaxation time, which can also be expressed as $\tau_B = (2\rho_p/9\rho_s)\tau_\eta$, with ρ_p the mass density of particles. If the mass density of particles is comparable with that of the solvent molecules, the two characteristic times τ_B and τ_η are of the same magnitude. It is obvious that on the time scale $t \gg \tau_B$, the velocities of particles relax to equilibrium. Therefore, the dynamics of colloidal suspensions can be determined solely by the configuration of particle positions, $P(\boldsymbol{r}^N, t)$, which is described by Smoluchowski equation [8, 9].

Moreover, we need to determine the characteristic time for the positions of colloidal particles to approach equilibrium, i.e., $\tau_I = a^2/D_0$, which is the time taken for a colloidal particle to diffuse a distance of its radius, usually 10^{-3}s or longer. On the other hand, one of the most important experimental methods to study colloidal suspensions is dynamic light scattering (DLS) [10], with the resolution being the order of 10^{-6}s . Since this time scale is much larger than τ_B and τ_η, Smoluchowski equation can well be applied to the dynamics of colloidal suspensions on all time scales related to DLS experiments.

One major characteristic quantity in the dynamics of colloidal systems is the average value of the square of particle displacements,

$$W(t) = \frac{1}{6}\left\langle (\boldsymbol{r}(t) - \boldsymbol{r}(0))^2 \right\rangle \qquad (2.6)$$

which is closely related to DLS measurements. For dilute systems with very small number density of particles, we obtain the following expression from Langevin equation

$$W(t) = D_0\left[t - \tau_B(1 - \mathrm{e}^{-t/\tau_B})\right] \qquad (2.7)$$

For $t \ll \tau_B$, $W(t) \approx (D_0/\tau_B)t^2$, implying that the motion of particles is similar to that of ideal gas molecules; while for $t \gg \tau_B$, $W(t) \approx D_0 t$, representing diffusion motion. However, for systems with higher number density of particles that can no longer be regarded as dilute, we have to distinguish between short-time and long-time behavior. The dynamics on the time scale $\tau_B \ll t \ll \tau_I$ is the short-time dynamics, where each colloidal particle diffuses by only a very smaller fraction of its own size. In this case the configuration of the system has almost not changed, so that the interaction potential remains unchanged. Therefore, only HI contributes to the dynamics of the particles. We may take one particle as representative and study its motion [11]. In a system which comprises of many particles, the motion of the representative particle is affected by the diffusion of other particles, which produce a flow field in the solvent even in a short time. This HI makes the short-time self-diffusion coefficient of the representative particle, D_S^S,[*] different from the diffusion coefficient of an isolated particle D_0. However, the diffusion of representative particle can still be expressed as $W(t) = D_S^S t$.

For $t \approx \tau_I$, the particle configuration is notably distorted, which results in the variance of interaction potential. This, correspondingly, leads to the change of direct interacting force and further influences the motion of the particle. The qualitative picture is that, after diffusing for some time, the representative particle moves towards a neighboring particle. However, this motion is slowed down due to the repulsion force, and the changing rate of $W(t)$ with time is sublinear. Meanwhile, the surrounding particles are also moving (In the sense of statistics, all particles in the system are equivalent), hence the configuration of the system is changed. Conclusively, on this time scale, the diffusion of representative particle is determined by both the potential force between particles and HI.

For $t \gg \tau_I$, the representative particle interacts simultaneously with many particles moving around. In this case, the colloidal suspension can be regarded as an effective fluid with larger viscosity coefficient, where the representative particle diffuses, i.e., $W(t) = D_S^L t$ .The long-time self-diffusion coefficient, D_S^L, is different with the short-time self-diffusion coefficient, D_S^S, due to the interaction between particles. From the above analysis it is realized that, dynamics on different time scales are based on different mechanisms, while DLS experiments can be used on all these time scales. In systems of interacting particles, $D_0 > D_S^S > D_S^L$. The diffusion tensor $\boldsymbol{D}_{ij}(\boldsymbol{r}^N)$ is a $3N \times 3N$ positive-definite super-matrix, which, in an infinitely dilute system, reduces to $\boldsymbol{D}_{ij}(\boldsymbol{r}^N) = D_0 \boldsymbol{I}\delta_{ij}$, where $\boldsymbol{I}$ is the three-order unit tensor.

It is not at all easy to calculate the diffusion tensor $\boldsymbol{D}_{ij}(\boldsymbol{r}^N)$ theoretically. A sophisticated means is "reflection theory" [2, 12], and in recent years some successful semi-analytical methods have been developed, such as multipole collocation method, etc. [13]. The difficulty in calculating the diffusion

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[*] This paper introduces several diffusion coefficients, which are all denoted by D. We assume that the subscripts of D represent diffusion properties, while the superscripts represent time scale, e.g., D_S^S means short-time self-diffusion coefficient, D_S^L long-time self-diffusion coefficient, D_C^S short-time collective diffusion coefficient, and D_C^L long-time collective diffusion coefficient, etc.

tensor originates from the many-body property of HI. When the volume fraction of colloidal particles is small, the average distance between particles is large, resulting in weak many-body correlation, so we can take account of only far-field contribution of two-body and three-body HI. In such circumstances, the fluid velocity $\boldsymbol{u}(\mathbf{r})$ can be expanded into Taylor series of r_{ij}^{-1}, with r_{ij} the distance between two particles i and j, and therefore $\boldsymbol{D}$ can also be Taylor expanded.

A powerful method for calculating the series expression of $\boldsymbol{D}$ is reflection theory, which is an iterative procedure from low to high orders. The basic idea is to first calculate the velocity of each particle independently, just as if no other particles exist, and then supplement the correction induced by the motion of other particles. Suppose that a force $\boldsymbol{F}_i$ is acted on particle i which has no acceleration. Since the total force operated on the particle is 0, it is easily deduced that the corresponding force experienced by the fluid is also $\boldsymbol{F}_i$. Further, suppose that the torque exerted on the fluid by the particle is $\boldsymbol{T}_i = 0$, while the velocity of the fluid at infinity is 0. All these conditions solely determine the translational velocity of the particle, and thus we can obtain the expression of translational diffusion tensor.

In one-body approximation, the particle moves independently in the fluid, being disturbed only by Stokes friction. However, in two-body approximation, two colloidal particles i and j are considered. The zero-order velocity of particle i produces the zero-order flow field $\boldsymbol{u}^{(0)}(\boldsymbol{r})$, the value of which at place j, $\boldsymbol{u}^{(0)}(\boldsymbol{r}_j)$, influences the motion of particle j, giving rise to the first-order correction to the velocity of particle j, $\upsilon_j^{(1)}$, which produces the flow field $\boldsymbol{u}^{(1)}(\boldsymbol{r})$, the value of which at place i gives rise to the second-order correction of the velocity of particle i, $\upsilon_i^{(2)}$, and so on. After many such iterations we arrive at the velocity of particle i as

$$\upsilon_i = \upsilon_i^{(0)} + \upsilon_i^{(2)} + \upsilon_i^{(4)} + \upsilon_i^{(6)} + \cdots \tag{2.8}$$

and the velocity of particle j as

$$\upsilon_j = \upsilon_j^{(1)} + \upsilon_j^{(3)} + \upsilon_j^{(5)} + \upsilon_j^{(7)} + \cdots \tag{2.9}$$

while the flow field at the position vector $\boldsymbol{r}$ as

$$\boldsymbol{u}(\boldsymbol{r}) = \boldsymbol{u}^{(0)}(\boldsymbol{r}) + \boldsymbol{u}^{(1)}(\boldsymbol{r}) + \upsilon^{(2)}(\boldsymbol{r}) + \cdots \tag{2.10}$$

Finally, from $\upsilon_j = \boldsymbol{D}_{ji}^{(2)}(\boldsymbol{r}_j - \boldsymbol{r}_i)\cdot\boldsymbol{F}_i$ and $\upsilon_i = \boldsymbol{D}_{ii}^{(2)}(\boldsymbol{r}_i - \boldsymbol{r}_j)\cdot\boldsymbol{F}_i$ we obtain the formula of the two-body diffusion tensor. As to the diagonal part of the matrix, since j can be any particle in the system except i, we should sum the expression over all particles except i to get the correct result.

In three-body approximation, one needs to consider three colloidal particles, denoted by i, j and l, respectively, where particle i moves with the velocity $\upsilon_i^{(0)}$, producing the fluid flow field $\boldsymbol{u}^{(0)}(\boldsymbol{r})$,which gives rise to the first-order correction of the velocity of particle j, $\upsilon_j^{(1)}$. Meanwhile, the motion of particle j also produces a new flow field, $\boldsymbol{u}^{(1)}(\boldsymbol{r})$, which can be interpreted as being reflected from the flow field of particle i. This field, however, further influences the motion of particle l, giving rise to the second-order correction to the velocity of particle l, $\upsilon_l^{(2)}$. In succession, the flow field $\boldsymbol{u}^{(2)}(\boldsymbol{r})$ brings the third-order correction to the velocity of particle i, $\upsilon_i^{(3)}$. And so forth, one may continue this procedure till the required order of the series expression of the diffusion tensor is obtained.

This method can easily be manipulated to get high order series of $1/r_{ij}$ by using computer algebra. The expansion up to more than 100 order of $1/r_{ij}$ is now available [14]. However, the expression including the first several orders is enough for most applications. Actually, in situations where a high order series is necessary (usually corresponding to high density systems), implying that many-body contributions cannot be neglected, one cannot really improve the final result by simply increasing the series orders. Here we present the expression up to $1/r_{ij}^7$ order:

$$\begin{aligned}
\frac{\boldsymbol{D}_{ii}}{D_0} &= \boldsymbol{I} + \sum_{j=1,\neq i}^{\infty}\left[\left(-\frac{15}{4}\left(\frac{a}{r_{ij}}\right)^4\right)\hat{\boldsymbol{r}}_{ij}\hat{\boldsymbol{r}}_{ij} - \frac{17}{16}\left(\frac{a}{r_{ij}}\right)^6\right. \\
&\quad \left.\cdot\left(\boldsymbol{I} - \frac{105}{17}\hat{\boldsymbol{r}}_{ij}\hat{\boldsymbol{r}}_{ij}\right) + O\left(\left(\frac{a}{r_{ij}}\right)^8\right)\right] \\
\frac{\boldsymbol{D}_{ij}}{D_0} &= \frac{3}{4}\frac{a}{r_{ij}}(\boldsymbol{I} + \hat{\boldsymbol{r}}_{ij}\hat{\boldsymbol{r}}_{ij}) + \frac{1}{2}\left(\frac{a}{r_{ij}}\right)^3(\boldsymbol{I} - 3\hat{\boldsymbol{r}}_{ij}\hat{\boldsymbol{r}}_{ij}) \\
&\quad + \frac{75}{4}\left(\frac{a}{r_{ij}}\right)^7\hat{\boldsymbol{r}}_{ij}\hat{\boldsymbol{r}}_{ij} + O\left(\left(\frac{a}{r_{ij}}\right)^8\right)
\end{aligned} \tag{2.11}$$

where the first order contribution of a/r_{ij}, $\boldsymbol{D}_{ij}$, is proportional to Oseen tensor, and the result including also $(a/r_{ij})^3$ is termed as Rodne-Prager tensor.

The first order contribution of $\boldsymbol{D}_{ii}^{(3)}$ is

$$\begin{aligned}
\boldsymbol{D}_{ii}^{(3)} &= -\frac{75}{16}D_{0,i}^{t}\sum_{j,l}^{N}{}'' \frac{a^7}{r_{ij}^2 r_{il}^2 r_{jl}^3}\hat{\boldsymbol{r}}_{ij}\hat{\boldsymbol{r}}_{il}[1 - 3(\hat{\boldsymbol{r}}_{ij}\cdot\hat{\boldsymbol{r}}_{jl})^2 - 3(\hat{\boldsymbol{r}}_{jl}\cdot\hat{\boldsymbol{r}}_{il})^2 \\
&\quad + 15(\hat{\boldsymbol{r}}_{jl}\cdot\hat{\boldsymbol{r}}_{il})^2(\hat{\boldsymbol{r}}_{ij}\cdot\hat{\boldsymbol{r}}_{jl})^2 - 6(\hat{\boldsymbol{r}}_{jl}\cdot\hat{\boldsymbol{r}}_{il})(\hat{\boldsymbol{r}}_{jl}\cdot\hat{\boldsymbol{r}}_{ij})(\hat{\boldsymbol{r}}_{ij}\cdot\hat{\boldsymbol{r}}_{il})]
\end{aligned} \tag{2.12}$$

where the notation “ 〃 ” in summation means that terms of $j = i$ and $l = j$ should be deducted to obtain the correct result. The higher order expressions of translational diffusion tensor can be calculated by similar procedures, here we just point out that the expressions including many orders are available in references [7, 15, 16].

3 Smoluchowski equation

In the previous section we noted that, at time scale $t \gg \tau_B$, the dynamics of colloidal systems can be determined solely by N-particle probability density distribution function, $P(\boldsymbol{r}^N, t)$, the evolution of which being described by Smoluchowski equation

$$\frac{\partial}{\partial t}P(\boldsymbol{r}^N,t)=\hat{O}(\boldsymbol{r}^N)P(\boldsymbol{r}^N,t) \tag{3.1}$$

where $\hat{O}(\boldsymbol{r}^N)$ is Smoluchowski operator defined as

$$\hat{O}(\boldsymbol{r}^N)=\sum_{i,j=1}^{N}\nabla_i\cdot\boldsymbol{D}_{ij}\cdot[\nabla_j+\beta\nabla_j U(\boldsymbol{r}^N)] \tag{3.2}$$

here $U(\boldsymbol{r}^N)$ denotes the direct interaction potential between colloidal particles, while the indirect interaction through solvent is comprised in the diffusion tensor $\boldsymbol{D}_{ij}(\boldsymbol{r}^N)$. $P(\boldsymbol{r}^N,t)$ represents the probability density at time t where colloidal particles constitute the configuration $\boldsymbol{r}^N$. In principle Smoluchowski equation can be reduced from Fork-Planck equation, which describes the probability distribution of colloidal particles. Actually, the reduction is the process of continuously integrating out the rapid variables. The mathematics involved is extremely complicated, and the approximations used in derivation are also unclear, hence we just present an heuristic derivation of the equation. This derivation, although not strict, gives out a plain physical picture. In the following we consider an N-particle system, and we assume that the particles undergo only the translational motion. P should satisfy the continuity equation due to the conservation of particle numbers, i.e.,

$$\frac{\partial}{\partial t}P(\boldsymbol{r}^N,t)+\sum_{i=1}^{N}\nabla_i\cdot(P(\boldsymbol{r}^N,t)\boldsymbol{\upsilon}_i)=0 \tag{3.3}$$

We have already known that, at the time scale $t\gg\tau_B\approx\tau_\eta$, the velocities of particles relax to equilibrium, implying that the net force exerted on each particle is zero

$$\boldsymbol{F}_i^P+\boldsymbol{F}_i^H+\boldsymbol{F}_i^B=0 \tag{3.4}$$

If no external force acts on the system, $\boldsymbol{F}_i^P=-\nabla_i U$ represents the interaction force between particles; $\boldsymbol{F}_i^H$ is hydrodynamic force, $\boldsymbol{F}_i^H=-\sum_{j=1}^{N}\xi_{ij}(\boldsymbol{r}^N)\cdot\boldsymbol{\upsilon}_j$, where ξ_{ij} is hydrodynamic friction tensor. $\boldsymbol{F}_i^B$ is termed as Brownian force, which originates from the principle of entropy increase, and drives the configuration of the system towards equilibrium. We will present its explicit formula later.

The generalized Stokes-Einstein relation

$$\sum_{l=1}^{N}\xi_{il}\cdot\boldsymbol{D}_{lj}=\kappa_{\mathrm{B}}T\boldsymbol{I}\delta_{ij} \tag{3.5}$$

leads to

$$\boldsymbol{v}_i=\beta\sum_{l=1}^{N}\boldsymbol{D}_{il}\cdot[-\nabla_l U+\boldsymbol{F}_l^B] \tag{3.6}$$

Inserting it into the continuity equation, one obtains

$$\frac{\partial}{\partial t}P(\boldsymbol{r}^N,t)+\sum_{i=1}^{N}\nabla_i\cdot\left(P(\boldsymbol{r}^N,t)\beta\sum_{l=1}^{N}\boldsymbol{D}_{il}\cdot[-\nabla_l U+\boldsymbol{F}_l^B]\right)=0 \tag{3.7}$$

By taking

$$\boldsymbol{F}_i^B=-\kappa_{\mathrm{B}}T\nabla_i\ln P(\boldsymbol{r}^N,t) \tag{3.8}$$

the condition that the probability density tends to equilibrium as $t\to\infty$, i.e.,

$$P_{eq}(\boldsymbol{r}^N)\propto\exp(-\beta U) \tag{3.9}$$

is satisfied, and in this way Smoluchowski equation is derived.

Defining the conditional probability density $P(\boldsymbol{r}^N,t\,|\,\boldsymbol{r}_0^N)$ as the probability density that at initial time t=0 the configuration of the system is $\boldsymbol{r}_0^N$ while at time t the configuration is $\boldsymbol{r}^N$, one derives that it is the solution of Smoluchowski equation under the initial condition

$$P(\boldsymbol{r}^N,t=0\,|\,\boldsymbol{r}_0^N)=\delta(\boldsymbol{r}^N-\boldsymbol{r}_0^N) \tag{3.10}$$

Hence the combined probability density can be expressed from the conditional probability density as

$$P(\boldsymbol{r}^N,t;\boldsymbol{r}_0^N,t=0)=P_{in}(\boldsymbol{r}_0^N)P(\boldsymbol{r}^N,t\,|\,\boldsymbol{r}_0^N,t=0) \tag{3.11}$$

with P_{in} $(\boldsymbol{r}_0^N)$ being the initial probability density at t=0. For systems in thermodynamic equilibrium, P_{in} is the same as the probability density of equilibrium state, P_{eq}. The formal solution of the conditional probability density can be expressed as

$$P(\boldsymbol{r}^N,t\,|\,\boldsymbol{r}_0^N,t=0)=\mathrm{e}^{\hat{O}t}\delta(\boldsymbol{r}^N-\boldsymbol{r}_0^N) \tag{3.12}$$

which, together with the initial probability density P_{eq}, determines the relevant dynamical quantity.

In a dilute system where there are no interactions between particles, one regards each particle as isolated. The probability of particle i being at position $\boldsymbol{r}_i$ at time t satisfies the following equation

$$\frac{\partial}{\partial t}P(\boldsymbol{r}_i,t)=D_0\nabla_i^2(\boldsymbol{r}_i,t) \tag{3.13}$$

By applying

$$P(\boldsymbol{r}^N,t)=\prod_{i=1}^{N}P(\boldsymbol{r}_i,t) \tag{3.14}$$

one easily derives the conditional probability density as

$$P(\boldsymbol{r},t\,|\,\boldsymbol{r}_0,t=0)=\frac{1}{(4\pi D_0 t)^{3/2}}\exp\left[-\frac{(\boldsymbol{r}-\boldsymbol{r}_0)^2}{4D_0 t}\right] \tag{3.15}$$

However, adjoint Smoluchowski operator, $\hat{O}_B$, is more commonly used in practice, which can be introduced through the study of several correlation function. Suppose that $f(\boldsymbol{r}^N)$ and $g(\boldsymbol{r}^N)$ are functions of the configuration $\boldsymbol{r}^N$, one defines the correlation function as

$$\langle f\,|\,g\rangle=\int\mathrm{d}\boldsymbol{r}^N P_{eq}(\boldsymbol{r}^N)f^*(\boldsymbol{r}^N)g(\boldsymbol{r}^N)\equiv\langle g\,|\,f\rangle^* \tag{3.16}$$

where P_{eq} is the equilibrium distribution of the system satisfying $\hat{O}P_{eq}=0$, and accordingly, $P_{eq}\propto\mathrm{e}^{-\beta U}(\boldsymbol{r}^N)$. This correlation function is interpreted as the inner product of the function $f(\boldsymbol{r}^N)$ and $g(\boldsymbol{r}^N)$, weighted by equilibrium distribution probability density. Another correlation function in use is an equal weighting inner product

$$(f\,|\,g)=\int\mathrm{d}\boldsymbol{r}^N f^*(\boldsymbol{r}^N)g(\boldsymbol{r}^N) \tag{3.17}$$

The adjoint Smoluchowski operator is defined by the following identity

$$(f\,|\,\hat{O}g)=(\hat{O}_B f\,|\,g) \tag{3.18}$$

Starting from Eqs. (3.2), (3.17) and (3.18), and through integration by part, one obtains

$$\hat{O}_B = \sum_{i,j=1}^{N} (\nabla_i - \beta \nabla_i U) \cdot \boldsymbol{D}_{ij} \cdot \nabla_j \tag{3.19}$$

It can also be proved through integration by part that, this operator is self-adjoint (Hermitian) in respect of the weighted inner product:

$$\langle f \,|\, \hat{O}_B g \rangle = \langle \hat{O}_B f \,|\, g \rangle \tag{3.20}$$

The following relation can easily be proved from Eqs. (3.10) and (3.18),

$$\langle f \,|\, \hat{O}_B g \rangle = -\sum_{i,j=1}^{N} \langle \nabla_i f^* \cdot \boldsymbol{D}_{ij} \cdot \nabla_j g \rangle_{eq} \tag{3.21}$$

which result is used to calculate the time correlation function of two dynamic variables $f(t) = f(\boldsymbol{r}^N(t))$ and $g(t) = g(\boldsymbol{r}^N(t))$. Since the stationary process is related only with the time interval, we take the initial point to be t=0 for convenience. Defining the time correlation function $C(t)$ as

$$C(t) \equiv \langle f(t=0) \,|\, g(t) \rangle \tag{3.22}$$

one gets

$$\begin{aligned} C(t) &\equiv \langle f(t=0) \,|\, g(t) \rangle \\ &= \int \mathrm{d}\boldsymbol{r}_0^N \int \mathrm{d}\boldsymbol{r}^N f^*(\boldsymbol{r}_0^N) g(\boldsymbol{r}^N) P(\boldsymbol{r}^N, t; \boldsymbol{r}_0^N, t=0) \\ &= \int \mathrm{d}\boldsymbol{r}_0^N f^*(\boldsymbol{r}_0^N) P_{eq}(\boldsymbol{r}_0^N) \int \mathrm{d}\boldsymbol{r}^N g(\boldsymbol{r}^N) \mathrm{e}^{\hat{O}t} \delta(\boldsymbol{r}^N - \boldsymbol{r}_0^N) \\ &= \int \mathrm{d}\boldsymbol{r}_0^N f^*(\boldsymbol{r}_0^N) P_{eq}(\boldsymbol{r}_0^N) \left[\mathrm{e}^{\hat{O}_B(\boldsymbol{r}^N)t} g(\boldsymbol{r}^N) \,|\, \delta(\boldsymbol{r}^N - \boldsymbol{r}_0^N) \right] \\ &= \int \mathrm{d}\boldsymbol{r}_0^N P_{eq}(\boldsymbol{r}_0^N) f^*(\boldsymbol{r}_0^N) \mathrm{e}^{\hat{O}_B(\boldsymbol{r}^N)t} g(\boldsymbol{r}_0^N) \\ &= \langle f \,|\, \mathrm{e}^{O_B t} g \rangle = \langle f^* \mathrm{e}^{O_B t} g \rangle_{eq} \end{aligned} \tag{3.23}$$

4 Equilibrium property, structure and interactions

Colloidal suspensions are unstable due to Van der Waals interactions between colloidal particles. For two colloidal spheres with a distance r, this Van der Waals interaction is given by Hamaker expression [17]

$$V_A(r) = -\frac{A}{6}\left[\frac{2a^2}{r^2 - 4a^2} + \frac{2a^2}{r^2} + \ln\left(1 - \frac{4a^2}{r^2}\right)\right] \tag{4.1}$$

where a denotes the radius of colloidal particles, and A is termed as Hamaker constant, with the order of magnitude of 10^{-20}J. This interaction is derived by summing over Van der Waals interactions between all parts of two colloidal particles. When two spheres are far away from each other, Eq. (4.1) becomes

$$V_A(r) = -\frac{16}{9} A \left(\frac{a}{r}\right)^6, \quad r \to \infty \tag{4.2}$$

while for two spheres very close to each other,

$$V_A(r) = -\frac{A}{12} \frac{a}{r - 2a}, \quad r \to 2a \tag{4.3}$$

If r is nearly $2a$, i.e., the two colloidal particles are very close to each other, they cannot be separated through thermal motion because of this very strong attraction and then coagulation occurs. There are two ways to avoid this coagulation instability, one is electrostatic stabilization method, which makes the surfaces of colloidal spheres with charge Q by treating the surfaces chemically. The electrostatic interaction between colloidal spheres in the solution can be described by Yukawa potential

$$V_c(r) = \begin{cases} \dfrac{Q_e^2}{\varepsilon r} \mathrm{e}^{-\kappa r}, & r > 2a \\ \infty, & r < 2a \end{cases} \tag{4.4}$$

where Q_e denotes the effective charge on colloidal sphere, usually different from Q. κ is *Debye* screening parameter, given by

$$\kappa^2 = \frac{4\pi}{\varepsilon \kappa_{\mathrm{B}} T} \sum_j \rho_j q_j^2 \tag{4.5}$$

with ε the dielectric constant of solution, and ρ_j and q_j the number density and charge of the ions in the solution, respectively. However, the situations in real systems are more complicated and κ is regarded as an adjustable parameter. Some simple statistical analysis leads to $Q_e = \dfrac{Q}{1+\kappa a} \mathrm{e}^{\kappa a}$, but in fact the relation between Q_e and Q is much more complicated. Another one is steric stabilization method. The short polymers are stuck onto the surfaces of colloidal spheres so that when colloidal spheres get closer no coagulation occurs because of the repulsion between polymer molecules.

The colloidal systems often used for scientific research are categorizes as:

1. Polystyrene, the most commonly used system in experiments. Polystyrene spheres are composed by polystyrene molecules, the hydrophilic end of which being on the surface of colloidal spheres. When putting the water in, the hydrophilic groups on the surface ionize, leaving it to be negatively charged. Polystyrene particles are spherical. For radius a>50 nm, the nonuniformity σ, defined as $\sigma = \dfrac{(\overline{a^2} - \overline{a}^2)^{1/2}}{\overline{a}}$, can be made to be approximately 0.01, with the refractive index $n_p \approx 1.60$. However, the refractive index of water is 1.33, very different from that of polystyrene. When the system is of high density, the polystyrene solution is usually opalescent due to multiple scattering.

Therefore, the density should be kept $\phi < 10^{-3}$ for light scattering experiments, while ϕ>0.3 for X-ray experiments.

2. Silica, also an electrically-stabilized colloidal material, where the radius of colloidal sphere is usually 10–500 nm, the nonuniformity σ being from 0.2 for small spheres to 0.02 for large spheres, the refractive index of $n_p \approx 1.45$, relatively fit for light scattering experiments.

3. PMMA(Polymethylmethacrylate), a kind of volume-stabilized colloidal system. For small PMMA colloidal spheres, the nonuniformity could be 0.1–0.2. While for spheres of radius a>150 nm, the nonuniformity could be $\sigma \approx 0.04$. The density of PMMA is approximately 1.19 g/cm^3,

with the refractive index 1.49.

In experiments, the volume fraction of colloidal suspensions, ϕ, needs to be determined precisely. A simple way is, from the given density of colloidal spheres and the density of solvent, by measuring the mass of the particles and solvent, the volume fraction is determined. However, this method cannot attain very high precision, mainly because the density of colloidal spheres may differ from that of the bulk material of which the colloidal spheres are made. Especially for volume-stabilized colloidal spheres, this difference is much larger. For dilute suspensions, by measuring shear viscosity coefficient and making use of Einstein relation [18]

$$\eta = \eta_0(1 + 2.5\phi + \cdots) \tag{4.6}$$

one obtains satisfactory results, where η and η_0 are the shear viscosity coefficient of colloidal suspensions and solvent, respectively.

The equilibrium properties of colloids are determined by statistical physics, with $U(\boldsymbol{r}_1, \boldsymbol{r}_2, \cdots, \boldsymbol{r}_N)$ being the interacting force between colloidal spheres, and $\boldsymbol{r}_i (i=1,2,\cdots,N)$ the coordinates of center of mass of N colloidal spheres. (For simplicity, we assume that the colloidal spheres are isotropic. In contrast, for anisotropic spheres, the relation between energy and orientation need to be further considered.) The spatial distribution of colloidal spheres is given by canonical distribution

$$P(\boldsymbol{r}_1, \boldsymbol{r}_2, \cdots, \boldsymbol{r}_N) = \frac{\mathrm{e}^{-\beta U}}{Z} \tag{4.7}$$

where

$$Z = \int \mathrm{d}\boldsymbol{r}_1 \mathrm{d}\boldsymbol{r}_2 \cdots \mathrm{d}\boldsymbol{r}_N \mathrm{e}^{-\beta U(\boldsymbol{r}_1, \boldsymbol{r}_2, \cdots, \boldsymbol{r}_N)} \tag{4.8}$$

is partition function. In many cases, one needs to know only the probability distribution of positions of $n(n \ll N)$ particles, rather than that of all N particles. Hence, one may introduce n-particle probability density

$$P^{(n)}(\boldsymbol{r}_1, \boldsymbol{r}_2, \cdots, \boldsymbol{r}_n) = \int \mathrm{d}\boldsymbol{r}_{n+1} \mathrm{d}\boldsymbol{r}_{n+2} \cdots \mathrm{d}\boldsymbol{r}_N P(\boldsymbol{r}_1, \boldsymbol{r}_2, \cdots, \boldsymbol{r}_N) \tag{4.9}$$

and define n-particle density function $\rho^{(n)}(\boldsymbol{r}_1, \boldsymbol{r}_2, \cdots, \boldsymbol{r}_n)$ as

$$\rho^{(n)}(\boldsymbol{r}_1, \boldsymbol{r}_2, \cdots, \boldsymbol{r}_n) \equiv \frac{N!}{(N-n)!} P^{(n)}(\boldsymbol{r}_1, \boldsymbol{r}_2, \cdots, \boldsymbol{r}_n) \tag{4.10}$$

The normalization relation for $P^{(n)}(\boldsymbol{r}_1, \boldsymbol{r}_2, \cdots, \boldsymbol{r}_n)$ leads to

$$\int \mathrm{d}\boldsymbol{r}^n \rho^{(n)}(\boldsymbol{r}_1, \boldsymbol{r}_2, \cdots, \boldsymbol{r}_n) = \frac{N!}{(N-n)!} \tag{4.11}$$

where for simplicity, we have used $\mathrm{d}\boldsymbol{r}^n$ to represent $\mathrm{d}\boldsymbol{r}_1 \mathrm{d}\boldsymbol{r}_2 \cdots \mathrm{d}\boldsymbol{r}_n$. In practice the most important situations are $n = 1$ and $n = 2$.

For a spatially uniform system, the probability distribution is translational invariant, i.e.,

$$P^{(n)}(\boldsymbol{r}_1 + \boldsymbol{a}, \boldsymbol{r}_2 + \boldsymbol{a}, \cdots, \boldsymbol{r}_n + \boldsymbol{a}) = P^{(n)}(\boldsymbol{r}_1, \boldsymbol{r}_2, \cdots, \boldsymbol{r}_n) \tag{4.12}$$

where $\boldsymbol{a}$ is an arbitrary vector. Therefore, $P^{(1)}(\boldsymbol{r}_1 + \boldsymbol{a}) = P^{(1)}(\boldsymbol{r}_1) = \text{constant}$ for $n = 1$, leading to

$$\begin{aligned} P^{(1)}(\boldsymbol{r}_1) &= \frac{1}{V} \\ \rho^{(1)}(\boldsymbol{r}_1) &\equiv \frac{N}{V} \equiv \rho \end{aligned} \tag{4.13}$$

with V the volume of the system and ρ the number density of colloidal particles of the system. For $n=2$, the probability distribution for a uniform system is

$$P^{(2)}(\boldsymbol{r}_1, \boldsymbol{r}_2) = P^{(2)}(\boldsymbol{r}_1 - \boldsymbol{r}_2) \tag{4.14}$$

More specifically, for an isotropic system, the formulae is further simplified as

$$P^{(2)}(\boldsymbol{r}_1, \boldsymbol{r}_2) = P^{(2)}(|\boldsymbol{r}_1 - \boldsymbol{r}_2|) \tag{4.15}$$

Now we introduce the concept of correlation length. When colloidal particles are far apart, the probability of finding an arbitrary particle is not influenced by other particles, or alternatively, the distribution of each particle is independent. On the contrary, a particle can “feel” the existence of other particles when they get closer, that is, they are correlated. We define the distance between particles from non-correlated to correlated as the correlation length ξ. Usually the correlation length ξ accords with the interaction range. Near the critical point, the correlation length diverges. When the distance between particles $r \gg \xi$,

$$P^{(n)}(\boldsymbol{r}_1, \boldsymbol{r}_2 \cdots, \boldsymbol{r}_n) = \prod_{i=1}^{n} P^{(1)}(\boldsymbol{r}_i) \tag{4.16}$$

and (noting that $n \ll N$)

$$\rho^{(n)}(\boldsymbol{r}_1, \boldsymbol{r}_2 \cdots, \boldsymbol{r}_n) = \prod_{i=1}^{n} \rho^{(1)}(\boldsymbol{r}_i) \tag{4.17}$$

Hence, n-particle distribution function is defined as

$$g^{(n)}(\boldsymbol{r}_1, \boldsymbol{r}_2 \cdots, \boldsymbol{r}_n) = \frac{\rho^{(n)}(\boldsymbol{r}_1, \boldsymbol{r}_2 \cdots, \boldsymbol{r}_n)}{\prod_{i=1}^{n} \rho^{(1)}(\boldsymbol{r}_i)} \tag{4.18}$$

where the most important situation being the two-particle distribution function

$$g(\boldsymbol{r}_1, \boldsymbol{r}_2) \equiv g^{(2)}(\boldsymbol{r}_1, \boldsymbol{r}_2) = \frac{\rho^{(2)}(\boldsymbol{r}_1, \boldsymbol{r}_2)}{\rho^{(1)}(\boldsymbol{r}_1)\rho^{(1)}(\boldsymbol{r}_2)} \tag{4.19}$$

For a uniformly isotropic system, two-particle distribution function

$$g(\boldsymbol{r}_1, \boldsymbol{r}_2) \equiv g(|\boldsymbol{r}_1 - \boldsymbol{r}_2|) = \frac{\rho^{(2)}(|\boldsymbol{r}_1 - \boldsymbol{r}_2|)}{\rho^2} \tag{4.20}$$

which, also termed as pair distribution function(PDF), has explicit physical meaning. It is proportional to the probability of finding a particle with a distance $|\boldsymbol{r}_1 - \boldsymbol{r}_2| = r$ away from another particle when the latter one is fixed (say, at $\boldsymbol{r}_2$). For $r \gg \xi$, there is no correlation between particles, so the probability of finding a particle is a constant. From the above definition it is known that the constant is taken as 1.

In very dilute limit, the pair distribution function can be written as

$$g(r) \equiv g^{(2)}(r) = \mathrm{e}^{-\beta u(r)} \tag{4.21}$$

where $u(r)$ is two-body interaction potential. For $\beta u(r) \gg 1$, $g(r) \approx 0$. For hard sphere colloids

$$u(r) = \begin{cases} \infty, & r > 2a \\ 0, & r < 2a \end{cases} \tag{4.22}$$

with $2a$ the diameter of colloidal sphere. Therefore, for $r < 2a$, $g(r) = 0$; while for $r \to \infty$, $g(r)=1$. Usually $g(r)$ has the form shown in Fig.1, wherein the value of $g(2a^{+})$ increases with the volume fraction. Under low-density approximation, $g(r)$ can also be approximated as

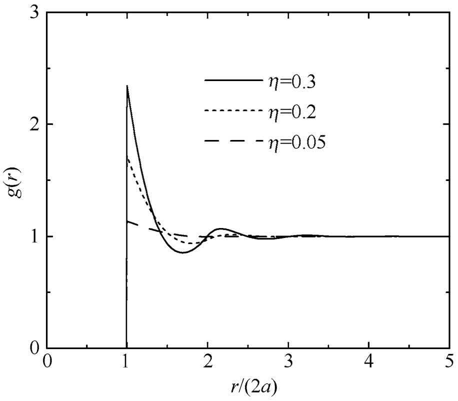

Fig. 1 The pair distribution function (PDF) $g(r)$ versus particle distance $r/(2a)$ of hard-sphere colloidal suspension by using Percus-Yevick method. The solid line corresponds to volume fraction $\phi=0.3$; the dashed line corresponds to volume fraction $\phi = 0.2$; and the dotted line corresponds to volume fraction $\phi = 0.05$.

$$g(r) = \theta(r-2a) \tag{4.23}$$

The PDF involves many thermodynamic information. The internal energy for a two-body interacting system is expressed as

$$\begin{aligned} U = \langle H \rangle &= \frac{3}{2} N\kappa_{\mathrm{B}}T + \frac{1}{2}\rho \int u(r)g(r)\mathrm{d}\mathbf{r} \\ &= \frac{3}{2} N\kappa_{\mathrm{B}}T + 2\pi\rho N \int \mathrm{d}r r^2 u(r)g(r) \end{aligned} \tag{4.24}$$

while the osmotic pressure of the colloidal system is

$$\begin{aligned} \frac{p}{\kappa_{\mathrm{B}}T} &= \rho - \frac{\beta}{3VZ}\int \mathrm{d}\mathbf{r}^N \left(\sum_{i,j} \frac{\partial u(r_{ij})}{\partial r_{ij}} \cdot r_{ij} \right) \mathrm{e}^{-\beta U} \\ &= \rho - \frac{\rho^2}{6\kappa_{\mathrm{B}}T}\int \mathrm{d}\mathbf{r} r u'(r)g(r) \\ &= \rho - \frac{2\pi\rho^2}{3\kappa_{\mathrm{B}}T}\int_0^{\infty} \mathrm{d}r r^3 u'(r)g(r) \end{aligned} \tag{4.25}$$

On the other hand, one obtains the following relation by calculating the fluctuation of the number of particles through grand canonical ensemble

$$\rho\int \mathrm{d}\mathbf{r}(g(r)-1) = \rho\kappa_{\mathrm{B}}T\chi_T - 1 \tag{4.26}$$

where

$$\chi_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T \equiv \frac{1}{\rho}\left(\frac{\partial \rho}{\partial p}\right)_T > 0 \tag{4.27}$$

is isothermal compressibility. Integrating the compressibility formula leads to the equation of state of the system, which conforms to Eq. (4.25), known as thermodynamic self-consistent relation, and can be used as a criterion to check all kinds of approximation methods.

The Fourier transform of PDF is related with the static structure factor by

$$\begin{aligned} S(q) &= 1 + \rho\int \mathrm{d}r \mathrm{e}^{-\mathrm{i}q\cdot r}(g(r)-1) \\ &= 1 + \frac{4\pi\rho}{q}\int_0^{\infty} \mathrm{d}r r \sin(qr)(g(r)-1) \end{aligned} \tag{4.28}$$

while the static structure factor can be measured by light scattering. For $q \to \infty, S(q) \to 1$. By making use of Eq. (4.27), one also obtains

$$\lim_{q\to 0} S(q) = \rho\kappa_{\mathrm{B}}T\chi_T \tag{4.29}$$

Numerical simulations can often be used to calculate PDF theoretically, such as Monte Carlo simulation, molecular dynamics simulation, density functional method and integration equation method, etc., among which the integration equation method is relatively simple and commonly used.

In addition to PDF, one may also introduce the so-called total correlation function $h(r) = g(r) - 1$. Obviously, $h(r) \to 0$ when $r \to \infty$. Theoretically, $h(r)$ represents the correlation of two particles a distance r apart. The direct correlation function $c(r)$ is accordingly introduced, with the relation to total correlation function being

$$h(r) = c(r) + \rho\int \mathrm{d}\mathbf{r}' c(\mathbf{r}-\mathbf{r}')h(r') \tag{4.30}$$

known as Ornstein-Zernike (OZ) equation [19]. This, however, can be interpreted as the definition of direct correlation function $c(r)$. A closure relation is required to calculate the correlations. The strict closure equation for two-body interacting system is

$$g(r) = \mathrm{e}^{-\beta u(r) - c(r) + h(r) + b(r)} \tag{4.31}$$

where $u(r)$ is the two-body interaction potential, while $b(r)$ is "bridge function". This closure relation can be derived by Mayer expansion, or equivalently, can be deduced from density functional theory. The term "bridge function" $b(r)$ originates from the *bridge graph* in the Mayer expansion. Ignoring $b(r)$ leads to the relation called hypernetted chain equation (HNC)

$$g(r) = \mathrm{e}^{-\beta u(r) - c(r) + h(r)} \tag{4.32}$$

On the other hand, one obtains Percus-Yevick(PY) equation by linearizing the formula with respect to $c(r)$- h(r) [20]

$$g(r) = \mathrm{e}^{-\beta u(r)}[1 - c(r) + h(r)] \tag{4.33}$$

PY equation gives out accurate result for hard-sphere colloids, while HNC equation offers better results for long-range interacting system. Various closure relations have been put forward to get more precise results, among which the most famous one is Rogers-Young(RY) equation [21]

$$g(r) = \mathrm{e}^{-\beta u(r)}\left(1 + \frac{\mathrm{e}^{f(r)[h(r)-c(r)]} - 1}{f(r)}\right) \tag{4.34}$$

where $f(r)=1-\mathrm{e}^{-\lambda r}$. The parameter λ introduced here is determined by thermodynamic self-consistent relation.

Furthermore, a simpler approximation can be applied to Yukawa potential under the low density limit, that is, mean sphere approximation (MSA)

$$c(r) = \mathrm{e}^{-\beta u(r)}, \quad r > 2a \tag{4.35}$$

Usually RY equation provides very nice results for systems of repulsive interaction, such as Yukawa potential.

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5 Short-time dynamics

The number density of colloidal particles in the suspension can be expressed as

$$\rho(\boldsymbol{r}) = \sum_{i=1}^{N} \delta(\boldsymbol{r} - \boldsymbol{r}_i) \tag{5.1}$$

with the Fourier transform

$$\rho(\boldsymbol{q}) = \sum_{i=1}^{N} \mathrm{e}^{-\mathrm{i}\boldsymbol{q}\cdot\boldsymbol{r}_i} \tag{5.2}$$

The time correlation function of this Fourier transform is defined as dynamic structure factor

$$S(q,t) = \frac{1}{N}\sum_{i,j=1}^{N} \left\langle \mathrm{e}^{\mathrm{i}\boldsymbol{q}\cdot[\boldsymbol{r}_i(0)-\boldsymbol{r}_j(t)]} \right\rangle_{eq} \tag{5.3}$$

which can be measured directly in DLS experiments, and plays a very important role in the study of colloidal dynamics. It is clear that dynamic structure factor is a special example of the time correlation function introduced in Section 3, where $f = g = \frac{1}{\sqrt{N}}\sum_{j=1}^{N} \mathrm{e}^{-\mathrm{i}\boldsymbol{q}\cdot\boldsymbol{r}_j} \equiv \frac{\rho(q)}{\sqrt{N}}$.

The initial slope of the correlation function $C(t)$ is derived from Eq. (3.23) as

$$\left.\frac{\mathrm{d}C(t)}{\mathrm{d}t}\right|_{t=0} = \langle f \mid \hat{O}_B g \rangle \tag{5.4}$$

where $t = 0$ denotes $\tau_B \ll t \ll \tau_I$. Hence the initial slope of $S(q, t)$ is determined by its first-order cumulant $\Gamma_1(q)$

$$\Gamma_1(q) = -\frac{\partial}{\partial t}\ln S(q,t)\bigg|_{t=0} = -\frac{1}{S(q)}\frac{\partial S(q,t)}{\partial t}\bigg|_{t=0} \tag{5.5}$$

where $S(q)=S(q, t = 0)$ is the static structure factor. Making use of Eqs. (3.23) and (5.4) one obtains

$$\begin{aligned}\Gamma_1(q) &= \frac{1}{NS(q)}\sum_{i,j=1}^{N}\left\langle \boldsymbol{q}\cdot\boldsymbol{D}_{ij}\cdot\boldsymbol{q}\mathrm{e}^{\mathrm{i}\boldsymbol{q}\cdot(\boldsymbol{r}_i-\boldsymbol{r}_j)}\right\rangle_{eq} \\ &= \frac{q^2}{NS(q)}\sum_{i,j=1}^{N}\left\langle \hat{\boldsymbol{q}}\cdot\boldsymbol{D}_{ij}\cdot\hat{\boldsymbol{q}}\mathrm{e}^{\mathrm{i}\boldsymbol{q}\cdot(\boldsymbol{r}_i-\boldsymbol{r}_j)}\right\rangle_{eq} \\ &\equiv q^2 D_{\mathrm{eff}}^S(q)\end{aligned} \tag{5.6}$$

with $\hat{\boldsymbol{q}}$ being the unit vector of direction $\boldsymbol{q}$. The factor here, $D_{\mathrm{eff}}^S(q)$, is termed as short-time effective diffusion coefficient, being

$$D_{\mathrm{eff}}^S(q) = D_0\frac{H(q)}{S(q)} \tag{5.7}$$

where $H(q)$ is hydrodynamic function, defined as

$$H(q) = \frac{1}{ND_0}\sum_{i,j=1}^{N}\left\langle \hat{\boldsymbol{q}}\cdot\boldsymbol{D}_{ij}\cdot\hat{\boldsymbol{q}}\mathrm{e}^{\mathrm{i}\boldsymbol{q}\cdot(\boldsymbol{r}_i-\boldsymbol{r}_j)}\right\rangle_{eq} \tag{5.8}$$

Since $H(q)$ involves the diffusion tensor $\boldsymbol{D}_{ij}$, and the calculation of taking ensemble average to equilibrium state as well, it is related with both the hydrodynamic interaction and the interaction potential between colloidal particles. Under dilute limit, each particle is regarded as isolated, and we thus take one as representative,

$$\begin{aligned}S(q,t) &= \left\langle \mathrm{e}^{\mathrm{i}\boldsymbol{q}\cdot(\boldsymbol{r}(t)-\boldsymbol{r}(0))}\right\rangle \\ &= \iint \mathrm{d}\boldsymbol{r}^N \mathrm{d}\boldsymbol{r}_0^N \mathrm{e}^{\mathrm{i}\boldsymbol{q}\cdot(\boldsymbol{r}-\boldsymbol{r}_0)} P(\boldsymbol{r}^N, t \,|\boldsymbol{r}_0^N) P_{eq}(\boldsymbol{r}_0^N)\end{aligned} \tag{5.9}$$

By using Eq. (3.15), this formula can be written as:

$$\begin{aligned}S(q,t) &= \int \mathrm{d}\boldsymbol{r}_0 \int \mathrm{d}\boldsymbol{r}\mathrm{e}^{\mathrm{i}\boldsymbol{q}\cdot(\boldsymbol{r}-\boldsymbol{r}_0)} \frac{1}{(4\pi D_0 t)^{3/2}} e - \frac{(\boldsymbol{r}-\boldsymbol{r}_0)^2}{4D_0 t} P_{eq}(\boldsymbol{r}_0) \\ &= \int \mathrm{d}\boldsymbol{r}_0 \mathrm{e}^{-q^2 D_0 t} P_{eq}(\boldsymbol{r}_0) \\ &= S(q)\mathrm{e}^{-q^2 D_0 t}\end{aligned} \tag{5.10}$$

where $S(q)=1$ is the static structure factor of non-interacting particle system.

If HI can be ignored, i.e., $\boldsymbol{D}_{ij} = D_0 \boldsymbol{I}\delta_{ij}$, then $H(q)=1$ is valid for any q, leading to $D_{\mathrm{eff}}^S(q) = D_0 / S(q)$, while any deviation of $H(q)$ from 1 implies that there is HI. If there are interactions between particles, $S(q) \ll 1$ when $q \ll q_m$, here q_m is the wave number corresponding to the maximum of $S(\boldsymbol{q})$, representing the average distance between particles. Therefore, $D_{\mathrm{eff}}^S(q) \gg D_0$ for $q \ll q_m$, implying that the particles diffuse very quickly. The particles diffuse most slowly at $q=q_m$. In short-time domain, and up to the first order of t, one obtains from Eqs. (5.5) and (5.6)

$$S(q,t) \approx S(q)\mathrm{e}^{-q^2 D_{\mathrm{eff}}^S t} \tag{5.11}$$

Experimentally, $S(q)$ can be measured by static light scattering (SLS); and $S(q,t)$ can be measured through DLS, producing the quantity $D_{\mathrm{eff}}^S(q)$. Thus, the hydrodynamic function $H(q)$ is measured by the combination of these two results. Figure 2 shows the theoretical and experimental results of $H(q)$ for HS colloidal systems. The curve of $H(q)$ is similar to the corresponding $S(q)$, only that the fluctuation in curve of $H(q)$ is smaller. The wave number corresponding to the peak of $H(q)$ is very close to q_m, and $H(q \ll q_m) < 1$. The value of $H(q \to 0)$ decreases when the volume fraction of the particles is increased, whether for HS or for charged particles.

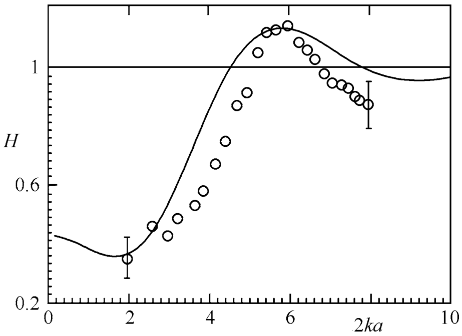

Fig.2 Experimental (*circle*) and theoretical (*solid line*) results of $H(q)$ for HS colloidal systems.

In two-body approximation, $H(q)$ is expressed as

$$D_0 H(q) = \langle \hat{\boldsymbol{q}} \cdot \boldsymbol{D}_{11} \cdot \hat{\boldsymbol{q}} \rangle + (N-1) \left\langle \hat{\boldsymbol{q}} \cdot \boldsymbol{D}_{12} \cdot \hat{\boldsymbol{q}} \mathrm{e}^{\mathrm{i}q\cdot(r_1 - r_2)} \right\rangle$$
$$= D_S^S + D_0 H_d(q) \qquad (5.12)$$

where D_S^S is obviously the short-time self-diffusion coefficient. For $q \gg q_m$, since the factor $\mathrm{e}^{\mathrm{i}q\cdot(r_1 - r_2)}$ vibrates rapidly, $H_d(q \gg q_m) \approx 0$. In the same limit, $S(q) \to 1$, therefore Eq.(5.7) leads to $D_{eff}^S(q \gg q_m) \approx D_0 H(q \gg q_m) \approx D_S^S$ i.e., $H(q \gg q_m) = \dfrac{D_S^S}{D_0}$. The ensemble average of Eq. (5.12) reduces to [22]

$$\langle f(\boldsymbol{r}_1 - \boldsymbol{r}_2) \rangle = \frac{1}{V} \int \mathrm{d}\boldsymbol{r} g(\boldsymbol{r}) f(\boldsymbol{r}), \qquad \boldsymbol{r} = \boldsymbol{r}_1 - \boldsymbol{r}_2 \qquad (5.13)$$

due to isotropy, where $g(r)$ is a pair distribution function. Because $g(r)$ depends on the type of interactions between particles and the volume fraction, the influence of HI to short-time diffusion coefficient $D_{\mathrm{eff}}^S(q)$ differs with systems. For charged particles, $g(r) = 0$ at the contact point of two spheres and for some distances thereafter, so only the first several terms in D_{ij} need to be taken into account. On the contrary, $g(r)$ attains its maximum at the contact point for HS system, implying that more terms in D_{ij} need to be included to get convergent result.

As an example, we present here the way to calculate hydrodynamic function. Considering the low-density situation where PDF can be approximated as

$$g(r) = \begin{cases} 1, & r > 2a \\ 0, & r < 2a \end{cases} \qquad (5.14)$$

together with Eqs. (5.12) and (5.13), one obtains the short-time self-diffusion coefficient

$$D_S = \langle \hat{\boldsymbol{q}} \cdot \boldsymbol{D}_{11} \cdot \hat{\boldsymbol{q}} \rangle \qquad (5.15)$$

Inserting Eq. (2.11) into the above formula, one has

$$\frac{D_S}{D_0} = 1 + \sum_{j=1,\neq i}^{\infty} \left[-\frac{15}{4} \left\langle \left(\frac{a}{r_{ij}} \right)^4 (\hat{\boldsymbol{r}}_{ij} \cdot \hat{\boldsymbol{q}})^2 \right\rangle - \frac{17}{16} \left\langle \left(\frac{a}{r_{ij}} \right)^6 \right\rangle + \frac{105}{17} \right.$$
$$\left. \left\langle \left(\frac{a}{r_{ij}} \right)^6 (\hat{\boldsymbol{r}}_{ij} \cdot \hat{\boldsymbol{q}})^2 \right\rangle + \cdots \right]$$

$$= 1 + \frac{N-1}{V} \left[-\frac{15}{4} \int \left(\frac{a}{r} \right)^4 \cos^2\theta g(r) r^2 \mathrm{d}r \mathrm{d}\cos\theta \mathrm{d}\phi \right.$$
$$-\frac{17}{16} \int \left(\frac{a}{r} \right)^6 g(r) r^2 \mathrm{d}r \mathrm{d}\cos\theta \mathrm{d}\phi + \frac{105}{16} \int \left(\frac{a}{r} \right)^6 \cos^2\theta$$
$$\left. \cdot g(r) r^2 \mathrm{d}r \mathrm{d}\cos\theta \mathrm{d}\phi + \cdots \right] \qquad (5.16)$$

which, by setting $x = \dfrac{r}{a}$ and taking the zero-order approximation of $g(r)$, becomes

$$\frac{D_S}{D_0} = 1 + 2\pi\rho a^3 \int_2^{\infty} \mathrm{d}x \left(-\frac{15}{4}\frac{2}{3}\frac{1}{x^2} - \frac{17}{16} 3 \frac{1}{x^4} + \frac{105}{16}\frac{2}{3}\frac{1}{x^4} + \cdots \right)$$
$$= 1 + 2\pi\rho a^3 \left(-\frac{5}{2}\frac{1}{2} - \frac{17}{8}\frac{1}{24} + \frac{35}{8}\frac{1}{24} + \cdots \right)$$
$$= 1 - \frac{111}{64}\phi = 1 - 1.734\phi \qquad (5.17)$$

Better results can be obtained by taking account of higher order terms of the expansion of two-body diffusion tensor Eq. (2.11) as

$$\frac{D_S}{D_0^t} = 1 - 1.831\phi \qquad (5.18)$$

It can be deduced from the expression of hydrodynamic function $H(q)$ that, HI plays a very important role in the calculation of the short-time diffusion coefficient [23, 24]. In charged-particle systems, strong repulsion pushes the particles as far away from each other as possible. However, the contribution of HI is $1/r$, with the range larger than that of the screened Coulumb interaction, which definitely influences the diffusion of particles.

We have discussed the situations where colloidal particles experience translational motion. In parallel, similar methods may be applied to study the rotational diffusion of suspended particles. However, the one-component colloidal suspensions of Brownian particles are systems that have been extensively investigated. Some theoretical results are presented in the following, which have taken account of three-body interaction. To make it clear, we denote the translational and rotational diffusion by the superscripts “t” and “r”, respectively. For HS systems with small volume fraction, the translational self-diffusion coefficient is [16, 25, 26]

$$\frac{D_S^{\mathrm{t},S}}{D_0^t} = 1 - 1.831\phi + 0.71\phi^2 \qquad (5.19)$$

and the rotational self-diffusion coefficient is [27]

$$\frac{D_S^{\mathrm{r},S}}{D_0^r} = 1 - 0.630\phi - 0.67\phi^2 \qquad (5.20)$$

while for charged-particle systems [27, 28]:

$$\frac{D_S^{\mathrm{t},S}}{D_0^t} = 1 - 2.59\phi^{1.30}$$
$$\frac{D_S^{\mathrm{r},S}}{D_0^r} = 1 - 1.2\phi^2 \qquad (5.21)$$

Recently, we have generalized the above results to two-component suspensions, where the volume fraction of one component is small. For HS systems, the self-diffusion coefficients for the component with low volume fraction are [29]

$$\frac{D_S^{\mathrm{t},s}}{D_0^t} = 1 + h_1^{\mathrm{t}}(\lambda)\phi + h_2^{\mathrm{t}}(\lambda)\phi^2$$

$$\frac{D_S^{\mathrm{r},s}}{D_0^r} = 1 + h_1^{\mathrm{r}}(\lambda)\phi + h_2^{\mathrm{r}}(\lambda)\phi^2$$

where $h_1(\lambda)$, $h_2(\lambda)$ are functions of λ , the radius ratio of the low fraction component (target) to high fraction component (host), and ϕ is the volume fraction of host particles. Figures 3, 4 show the relations of self-diffusion coefficients of the target component to the volume fraction of the host component for various values of λ . It is obvious that the system conforms to the one-component case for $\lambda = 1$.

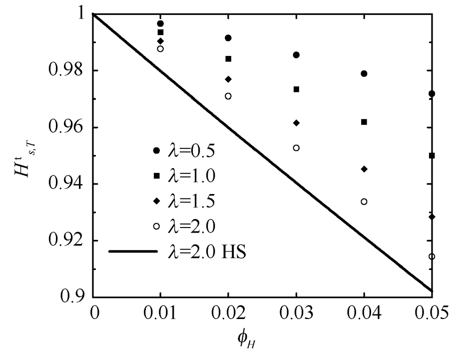

Fig. 3 The normalized short-time translational self-diffusion coefficient $H^{\mathrm{t}}_{s,T} = D^{\mathrm{t}}_{s,T} / D^{\mathrm{t}}_0$ versus the volume fraction of host particles, ϕ . The parameters of the system are: dielectric constant $\varepsilon = 78$, temperature *T*=300 K, the diameter of representative particle σ_T = 100 nm, the volume fraction ϕ_T =10^{-5}, the effective charge $Z_T = Z_H$ = 200 (with unit *e*). The filled circle corresponds to the situation of λ = 0.5, the filled square to λ =1.0, the filled diamond to λ =1.5, and the open circle denotes the situation of λ =2.0. The straight line represents the short-time translational self-diffusion coefficient of HS system when λ =2.0.

Starting from Eqs. (5.7) and (5.10), one defines the short-time collective diffusion coefficient as

$$D_C^S = \lim_{q\to 0} D_{\mathrm{eff}}^S(q) = D_0 \frac{H(q\to 0)}{S(q\to 0)} \tag{5.22}$$

while for $q \ll q_m$ and $t \ll \tau_I$,

$$S(q,t) \approx S(q)\mathrm{e}^{-q^2 D_C^S t}$$
(5.23)

From the definition it is realized that *S*(*q*,*t*) is the correlation function of density fluctuation of the wavelength $\propto 1/q$. The wavelength is very large for $q \to 0$, therefore D_C^S represents the initial relaxation of density fluctuation in macroscopic scale.

In order to calculate short-time collective diffusion coefficient, one needs the long-wave limit result of $H_d(q)$ and *S*(*q*), where $H_d(q)$ can be calculated as follows.

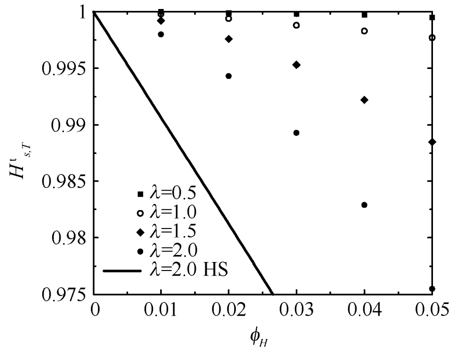

Fig. 4 The normalized short-time rotational self-diffusion coefficient $H^{\mathrm{r}}_{s,T} = D^{\mathrm{r}}_{s,T} / D^{\mathrm{r}}_0$ versus the volume fraction of host particles, ϕ . The parameters of the system are: dielectric constant ε =78, temperature *T*=300 K, the diameter of representative particle σ_T =100 nm, the volume fraction ϕ_T =10^{-5}, the effective charge Z_T= Z_H= 200 (with unit *e*). The filled square corresponds to the situation of λ = 0.5, the open circle to λ = 1.0, the filled diamond to λ =1.5, and the filled circle denotes the situation of λ =2.0. The straight line represents the short-time rotational self-diffusion coefficient of HS system when λ =2.0.

Starting from Eqs. (5.12) and (5.13), and then inserting them into the second equality of Eq.(2.11), one gets

$$\begin{aligned} H_d(q) = \rho\hat{\boldsymbol{q}} \cdot \left[\int \mathrm{d}\boldsymbol{r} \frac{3}{4}\left(\frac{a}{r}\right)(\boldsymbol{I} + \hat{\boldsymbol{r}}\hat{\boldsymbol{r}})\mathrm{e}^{\mathrm{i}\boldsymbol{q}\cdot\boldsymbol{r}}(g(r)-1) \right] \cdot \hat{\boldsymbol{q}} + \rho\hat{\boldsymbol{q}} \\ \cdot \left[\int \mathrm{d}\boldsymbol{r} \frac{3}{4}\left(\frac{a}{r}\right)(\boldsymbol{I} + \hat{\boldsymbol{r}}\hat{\boldsymbol{r}})\mathrm{e}^{\mathrm{i}\boldsymbol{q}\cdot\boldsymbol{r}} \right] \cdot \hat{q} + \rho \int r^2 \mathrm{d}r\mathrm{d}\cos\theta\mathrm{d}\phi g(r) \\ \cdot \left[\frac{1}{2}\left(\frac{a}{r}\right)^3 (1 - 3\cos^2\theta) + \frac{75}{4}\left(\frac{a}{r}\right)^7 \cos^2\theta \right] \mathrm{e}^{\mathrm{i}qr\cos\theta} \end{aligned} \tag{5.24}$$

To make the first integral convergent, one has to subtract 1 from *g*(*r*), the result of which can be compensated by adding the second term. The integral in the second term is the Fourier transform of Oseen tensor, the result of which being proportional to $\frac{1}{q^2}(\boldsymbol{I} - \hat{\boldsymbol{q}}\hat{\boldsymbol{q}})$. Since $\hat{\boldsymbol{q}} \cdot (\boldsymbol{I} - \hat{\boldsymbol{q}}\hat{\boldsymbol{q}}) \cdot \hat{\boldsymbol{q}} = 0$, the second term in the above formula is 0. Note that

$$\int \mathrm{d}\cos\theta\mathrm{d}\phi\mathrm{e}^{\mathrm{i}qr\cos\theta} = 4\pi j_0(qr)$$

$$\int \mathrm{d}\cos\theta\mathrm{d}\phi\cos^2\theta\mathrm{e}^{\mathrm{i}qr\cos\theta} = -4\pi\left[j_2(qr) - \frac{j_1(qr)}{qr} \right] \tag{5.25}$$

where $j_n(qr)$ is spherical Bessel function of *n*th-order. Making use of $\frac{j_1(x)}{x} = \frac{1}{3}[j_2(x) + j_0(x)]$, and taking the low-density approximation *g*(*r*)=θ(*r*−2*a*), further applying transformation with *x*=*r*/*a*, one obtains

$$H_d(q) = -4\pi\rho a^3 \int_0^2 \mathrm{d}xx\left[j_0(qax) - \frac{1}{2} j_2(qax) \right]$$

$$+4\pi\rho a^3\int_2^\infty \mathrm{d}x\frac{1}{x}j_2(qax)$$

$$+4\pi\rho a^3\int_2^\infty \mathrm{d}x\frac{25}{4x^5}[j_0(qax)-2j_2(qax)] \qquad (5.26)$$

where the integrals can be evaluated analytically. However, here we just present the result under long-wavelength limit and figures, rather than giving out the complicated analytical expression. For $q\to 0, j_0(qax)\to 1, j_1(qax)\to\frac{1}{3}qax,$ $j_2(qax)\to\frac{1}{15}(qax)^2$. The first term in the above formula then becomes $-3\pi\rho a^3\cdot\frac{4}{3}\cdot 2=-6\phi$, and the third term becomes $4\pi\rho a^3\cdot\frac{25}{4}\cdot\frac{1}{64}=\frac{75}{256}\phi$. However, one should be very careful with the second term. If directly inserting the asymptotic expression of $j_2(qax)$ into the formula, the integral diverges. On the other hand, if at first taking the limit $q\to 0$, the integral becomes zero. Recognizing that the limit $q\to 0$ is related with the fact that the whole system tends towards infinity, while the real systems are always finite; therefore the limit $q\to 0$ should be taken after the calculation is finished. Noticing that

$$\begin{aligned}\int_2^\infty \mathrm{d}x\frac{1}{x}j_2(qax)&=\int_0^\infty \mathrm{d}x\frac{j_2(x)}{x}-\int_0^2 \mathrm{d}x\frac{j_2(qax)}{x}\\&=\frac{1}{3}-\int_0^2 \mathrm{d}x\frac{1}{x}\frac{(qax)^2}{15}\to\frac{1}{3}\end{aligned} \qquad (5.27)$$

the second term yields $4\pi\rho a^3\frac{1}{3}=\phi$. Hence the result of $H_d(q)$ under long-wavelength limit is

$$H_d(q\to 0)=-6\phi+\frac{75}{256}\phi+\phi=-4.707\phi \qquad (5.28)$$

with the precise two-body results being $H_d(q\to 0)=-4.72\phi$, and $H(q\to 0)=-(1.83+4.72)\phi=-6.55\phi$. Figure 5 shows the curve of $H_d(q)$ as a function of qa, from which it can be seen that $H_d(q)\to 0$ for $qa\gg 1$.

At last, we present here the result of static structure factor $S(q)$ under low-density limit

$$S(q)=1+\rho\int \mathrm{d}\boldsymbol{r}(g(r)-1)\mathrm{e}^{-\mathrm{i}\boldsymbol{q}\cdot\boldsymbol{r}} \qquad (5.29)$$

Since the above integral is proportional to ρ (and accordingly proportional to ϕ), we simply need to take the zero-order approximation of $g(r)$, thereby yielding

$$\begin{aligned}S(q)&=1-\rho\int_0^{2a}r^2\mathrm{d}r\int \mathrm{e}^{\mathrm{i}qr\cos\theta}d\theta\\&=1-3\phi\int_0^2 \mathrm{d}x x^2\frac{\sin(qax)}{qax}\\&=1-3\frac{\sin(2qa)-2qa\cos(2qa)}{(qax)^3}\phi\end{aligned} \qquad (5.30)$$

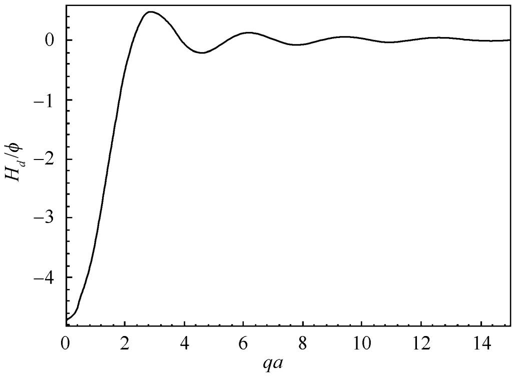

Fig. 5 The theoretical result of H_d (q) (as a function of qa) for HS suspensions.

For $q\to 0$, $S(q)=1-8\phi$. Inserting the results into Eq. (5.22) leads to

$$D_c^S=D_0\frac{1-6.55\phi}{1-8\phi}=D_0(1+1.45\phi) \qquad (5.31)$$

6 Long-time dynamics

6.1 Phenomenological Treatment

The concept of long-time refers to the time scale $t\gg\tau_I$. Since τ_I is the characteristic time when the configuration of system changes remarkably, the effect of collective motion should be taken into account in the long-time dynamics. It is known from experiments that, usually dynamical structure factor $S(q,t)$ is not an exponentially-decaying function [30]. However, in hydrodynamic limit (i.e., $q\ll q_m, t\gg\tau_I$), the motion of particles satisfy the local continuity equation:

$$\frac{\partial}{\partial t}\bar{\rho}(\boldsymbol{r},t)+\nabla\cdot\bar{\boldsymbol{j}}(\boldsymbol{r},t)=0 \qquad (6.1)$$

where $\bar{\rho}(\boldsymbol{r},t)$ and $\bar{\boldsymbol{j}}(\boldsymbol{r},t)$ are coarse-grain average of number density and particle flow, respectively, for volume $\Delta V\gg q_m^{-3}$. By applying local Fick' s law

$$\bar{\boldsymbol{j}}(\boldsymbol{r},t)=-D_C^L\nabla\bar{\rho}(\boldsymbol{r},t) \qquad (6.2)$$

one obtains

$$\rho(\boldsymbol{q},t)=\rho(\boldsymbol{q},0)\exp[-q^2D_C^Lt] \qquad (6.3)$$

with D_C^L the long-time collective diffusion coefficient. Consequently, the dynamic structure factor is derived as

$$S(q,t)=S(q)\mathrm{e}^{-q^2D_C^Lt} \qquad (6.4)$$

where $S(q)=S(q, t=0)$ is the static structure factor. That is to say, in hydrodynamic limit, $S(q, t)$ decays exponentially with time. DLS experiments can resolve the situation far away from this limit, therefore we must discuss the case where $q\approx q_m$ and $t\gg\tau_I$. Generalizing Eq. (6.2) to both temporally and spatially nonlocal cases, one has

$$\boldsymbol{j}(\boldsymbol{r},t)=-\int_0^t \mathrm{d}t'\int \mathrm{d}\boldsymbol{r}'\boldsymbol{D}_C(|\boldsymbol{r}-\boldsymbol{r}'|,t-t')\cdot\nabla'\rho(\boldsymbol{r}',t') \tag{6.5}$$

The diffusion function $\boldsymbol{D}_C(\boldsymbol{r},t)$ introduced here is the phenomenological generalization of the diffusion coefficient D_C. Because of the spatial translational invariance and isotropy it is solely determined by $|\boldsymbol{r}-\boldsymbol{r}'|$. The particle flow density at point $(\boldsymbol{r},t)$ is relevant with the density gradient at surrounding points $(\boldsymbol{r}',t'<t)$.

Now we discuss the influence of nonlocality to diffusion motion. Again starting from continuity equation

$$\frac{\partial}{\partial t}\rho(\boldsymbol{q},t)+\mathrm{i}\boldsymbol{q}\cdot\boldsymbol{j}(\boldsymbol{q},t)=0 \tag{6.6}$$

where $\rho(\boldsymbol{q},t)=\sum_{l=1}^{N}\mathrm{e}^{-\mathrm{i}\boldsymbol{q}\cdot\boldsymbol{r}_l(t)}$, $\boldsymbol{j}(\boldsymbol{q},t)=-\int_0^t \mathrm{d}t' D_C(q,t-t')\cdot\mathrm{i}\boldsymbol{q}\,\rho(\boldsymbol{q},t')$, and implementing Laplace transform to Eq. (6.6), one obtains

$$s\tilde{\rho}(\boldsymbol{q},s)-\rho(\boldsymbol{q},0)=-\boldsymbol{q}\cdot\tilde{\boldsymbol{D}}_C(q,s)\cdot\boldsymbol{q}\tilde{\rho}(\boldsymbol{q},s) \tag{6.7}$$

Hence the Laplace transform of dynamic structure factor is derived as

$$\tilde{S}(q,s)=\frac{1}{N}\langle\rho(\boldsymbol{q},0)\,|\,\tilde{\rho}(\boldsymbol{q},s)\rangle=\frac{S(q)}{s+q^2\tilde{D}_C(q,s)} \tag{6.8}$$

where

$$\tilde{D}_C(q,s)=\hat{\boldsymbol{q}}\cdot\boldsymbol{D}_C(q,s)\cdot\hat{\boldsymbol{q}} \tag{6.9}$$

In hydrodynamic limit $s\to 0, q\to 0$, the Fourier-Laplace transform of Eq. (6.5) becomes

$$\tilde{\boldsymbol{j}}(\boldsymbol{q},s)=-\mathrm{i}\boldsymbol{D}_C^L\cdot\boldsymbol{q}\rho(\boldsymbol{q},s) \tag{6.10}$$

where

$$D_C^L=\lim_{q\to 0}\lim_{s\to 0}\boldsymbol{D}_C(\boldsymbol{q},s) \tag{6.11}$$

that is to say, the nonlocal relation reduces to local Fick's law in hydrodynamic limit. However, generally, $\tilde{\boldsymbol{D}}_C(q,s)$ is related with q and s, so that dynamic structure factor deviates from the simple exponentially decaying relation.

Recall that the short-time effective diffusion coefficient is already given through Eq. (5.6), which is $D_{\mathrm{eff}}^S(\boldsymbol{q})=D_0H(q)/S(q)$. By expressing the retardation term in generalized Fick's law as $\Delta\tilde{D}_C(q,s)=\tilde{D}_C(q,s)-D_{\mathrm{eff}}^S(q)$, and defining an important quantity $\tilde{M}_C(q,s)$ from

$$q^2\Delta\tilde{D}_C(q,s)=-\tilde{M}_C(q,s)/S(q) \tag{6.12}$$

one expresses Eq. (6.8) as

$$\tilde{S}(q,s)=\frac{S(q)}{s+\dfrac{1}{S(q)}\left(\omega(q)-\tilde{M}_C(q,s)\right)} \tag{6.13}$$

with $\omega(q)\equiv q^2D_0H(q)$. The subscript "C" here in $\tilde{M}_C(q,s)$ represents collective diffusion. Carrying out the inverse Laplace transformation, one gets

$$\frac{\partial S(q,t)}{\partial t}=-\omega(q)\frac{S(q,t)}{S(q)}+\int_0^t \mathrm{d}t' M_C(q,t-t')\frac{S(q,t')}{S(q)} \tag{6.14}$$

which is just the memory equation of dynamic structure factor. At short-time, the integral term can be neglected, leading to the same expression as shown before. But for longer time when $t\approx\tau_I$, the contribution of this memory term cannot be ignored so that $\frac{\partial S(q,t)}{\partial t}$ depends not only on $S(q,t)$, but on the condition at time $t'\leqslant t$ as well. This memory effect can be calculated by memory function $M_C(q,t)$.

6.2 The microscopic theory

We have just deduced the memory equation (6.14) from phenomenological relations. However, this equation can equivalently be derived strictly from microscopic theory [11, 31], which, in addition, yields the microscopic expression of the memory function $M_C(q,t)$. The basic starting point is the conservation of the number of colloidal particles, i.e., the number density satisfies the continuity equation

$$\frac{\partial}{\partial t}\rho(\boldsymbol{q},t)=-\mathrm{i}\boldsymbol{q}\cdot\boldsymbol{j}_\rho(\boldsymbol{q}) \tag{6.15}$$

where $\boldsymbol{j}_\rho(\boldsymbol{q})$ is the particle flow density. The condition $q\to 0$ leads to

$$\frac{\partial}{\partial t}\rho(\boldsymbol{q},t)\to 0 \tag{6.16}$$

so the conserved quantity is also termed "slow variable" (at least for $q\to 0$). The one-dimensional sub-space spanned by density function is called sub-space of dynamic slow variable. Except for the number density, all of the other variables approach equilibrium very quickly, thus known as rapid variables. Obviously, dynamic structure factor is just the correlation of this slow variable. Since it is coupled with other variables, each dynamic variable can be divided into rapid and slow parts. Introducing scalar project operator $\hat{P}(\boldsymbol{q})$, which projects out the slow part of any dynamical variable A

$$\hat{P}A=\rho(\boldsymbol{q})\frac{\langle\rho(\boldsymbol{q})\,|\,A\rangle}{\langle\rho(\boldsymbol{q})\,|\,\rho(\boldsymbol{q})\rangle} \tag{6.17}$$

The complementary operator of $\hat{P}$,

$$\hat{Q}=1-\hat{P} \tag{6.18}$$

projects the variable to the complementary subspace constituted by rapid variables. Thus $\hat{Q}A$ is the rapid part of dynamical variable A. Here $\langle\cdots|\cdots\rangle$ represents the inner product defined by Eq. (3.16). The project operator $\hat{P}$ and $\hat{Q}$ satisfy the following explicit relations

$$\begin{aligned}&\hat{P}\hat{P}A=\hat{P}A\\&\hat{Q}\hat{Q}A=\hat{Q}A\\&\hat{P}\hat{Q}A=\hat{Q}\hat{P}A=0\end{aligned} \tag{6.19}$$

The inner product of operators $\hat{P}$ and $\hat{Q}$ has the following properties. Supposing that A and B are two arbitrary dynamical quantities, then

$$\begin{aligned}\left\langle \hat{P}A \mid \hat{Q}B \right\rangle &= \left\langle \frac{\langle \rho \mid A\rangle}{\langle \rho \mid \rho\rangle}\rho \,\Big|\, \left(B - \frac{\langle \rho \mid B\rangle}{\langle \rho \mid \rho\rangle}\rho \right)\right\rangle \\ &= \frac{\langle \rho \mid A\rangle}{\langle \rho \mid \rho\rangle}\langle \rho \mid B\rangle - \frac{\langle \rho \mid A\rangle}{\langle \rho \mid \rho\rangle}\frac{\langle \rho \mid B\rangle}{\langle \rho \mid \rho\rangle}\langle \rho \mid \rho\rangle \equiv 0\end{aligned} \tag{6.20}$$

Similarly,

$$\left\langle \hat{Q}A \mid \hat{P}B \right\rangle = 0 \tag{6.21}$$

$$\begin{aligned}\left\langle \hat{P}A \mid \hat{P}B \right\rangle &= \left\langle \frac{\langle \rho \mid A\rangle}{\langle \rho \mid \rho\rangle}\rho \,\Big|\, \frac{\langle \rho \mid B\rangle}{\langle \rho \mid \rho\rangle}\rho \right\rangle \\ &= \frac{\langle \rho \mid A\rangle}{\langle \rho \mid \rho\rangle}\langle \rho \mid B\rangle = \left\langle \hat{P}A \mid B \right\rangle = \left\langle A \mid \hat{P}B \right\rangle\end{aligned} \tag{6.22}$$

and

$$\left\langle \hat{Q}A \mid \hat{Q}B \right\rangle = \left\langle \hat{Q}A \mid B \right\rangle = \left\langle A \mid \hat{Q}B \right\rangle \tag{6.23}$$

From the definition the dynamic structure factor is expressed as

$$\begin{aligned}S(q,t) &= \frac{1}{N}\langle \rho(-\boldsymbol{q},0)\rho(\boldsymbol{q},t)\rangle_{eq} \\ &= \frac{1}{N}\langle \rho(-\boldsymbol{q},0)\mathrm{e}^{O_B t}\rho(\boldsymbol{q},0)\rangle_{eq}\end{aligned} \tag{6.24}$$

where O_B is the adjoint Smoluchowski operator. Differentiating the expression with respect to time leads to

$$\begin{aligned}\frac{\partial S(q,t)}{\partial t} &= \frac{1}{N}\langle \rho(-\boldsymbol{q},0)\mathrm{e}^{O_B t}O_B\rho(\boldsymbol{q},0)\rangle_{eq} \\ &= \frac{1}{N}\langle \rho(-\boldsymbol{q},0)\mathrm{e}^{O_B t}\hat{P}O_B\rho(\boldsymbol{q},0)\rangle_{eq} \\ &\quad + \frac{1}{N}\langle \rho(-\boldsymbol{q},0)\mathrm{e}^{O_B t}\hat{Q}O_B\rho(\boldsymbol{q},0)\rangle_{eq}\end{aligned} \tag{6.25}$$

Making transformation to the first term,

$$\mathrm{e}^{O_B t}\hat{P}O_B\rho(\boldsymbol{q},0) = \mathrm{e}^{O_B t}\rho\frac{\langle \rho \mid O_B\rho\rangle}{\langle \rho \mid \rho\rangle} \equiv \Omega(\boldsymbol{q})\mathrm{e}^{O_B t}\rho(\boldsymbol{q},0) \tag{6.26}$$

where

$$\mathit{\Omega}(\boldsymbol{q}) = \frac{\langle \rho(\boldsymbol{q},0) \mid O_B\rho(\boldsymbol{q},0)\rangle}{\langle \rho(\boldsymbol{q},0) \mid \rho(\boldsymbol{q},0)\rangle}$$

and inserting Eq. (5.7) into the formula, one obtains

$$\mathit{\Omega}(\boldsymbol{q}) = -q^2 D_{\mathrm{eff}}^S(q) = -q^2 D_0\frac{H(q)}{S(q)} = -\frac{\omega(q)}{S(q)} \tag{6.27}$$

For simplicity, we have omitted the arguments of $\rho(\boldsymbol{q},0)$ in the foregoing derivation. This, however, can be easily resumed in the final result, according to the context.

An operator identity is needed to calculate the second term,

$$\mathrm{e}^{O_B t} = \mathrm{e}^{\hat{Q}O_B t} + \int_0^t \mathrm{d}t'\mathrm{e}^{O_B(t-t')}\hat{P}O_B\mathrm{e}^{\hat{Q}O_B t'} \tag{6.28}$$

the proof of which is as follows. Introducing

$$\mathit{\Delta}(t) = \mathrm{e}^{O_B t} - \mathrm{e}^{\hat{Q}O_B t} \tag{6.29}$$

the first derivative of which being

$$\frac{\mathrm{d}\mathit{\Delta}}{\mathrm{d}t} = O_B\mathrm{e}^{O_B t} - \hat{Q}O_B\mathrm{e}^{\hat{Q}O_B t} = O_B\mathit{\Delta} + \hat{P}O_B\mathrm{e}^{\hat{Q}O_B t} \tag{6.30}$$

one finds the solution as

$$\mathit{\Delta}(t) = \int_0^t \mathrm{d}t'\mathrm{e}^{O_B(t-t')}\hat{P}O_B\mathrm{e}^{\hat{Q}O_B t'} \tag{6.31}$$

which conforms to Eq. (6.28).

Defining $R(\boldsymbol{q},t) = \mathrm{e}^{\hat{Q}(\boldsymbol{q})O_B t}\hat{Q}(\boldsymbol{q})O_B\rho(\boldsymbol{q},t)$, one obtains

$$\begin{aligned}\mathrm{e}^{O_B t}\hat{Q}O_B\rho &= \mathrm{e}^{\hat{Q}O_B t}\hat{Q}O_B\rho + \int_0^t \mathrm{d}t'\mathrm{e}^{O_B(t-t')}\hat{P}O_B\mathrm{e}^{QO_B t'}\hat{Q}O_B\rho \\ &= R(t) + \int_0^t \mathrm{d}t'\mathrm{e}^{O_B(t-t')}\hat{P}O_B R(t')\end{aligned} \tag{6.32}$$

Further noticing that $R(\boldsymbol{q}, t)$ is a rapid variable satisfying $\hat{Q}R = R$, and by making use of Eqs. (6.20)–(6.23), the integrand in Eq. (6.32) can be transformed as

$$\begin{aligned}\hat{P}O_B R(t) &= \rho\frac{\langle \rho \mid O_B R(t)\rangle}{\langle \rho \mid \rho\rangle} = \rho\frac{\langle O_B\rho \mid R(t)\rangle}{\langle \rho \mid \rho\rangle} \\ &= \rho\frac{\langle O_B\rho \mid \hat{Q}R(t)\rangle}{\langle \rho \mid \rho\rangle} = \rho\frac{\langle \hat{Q}O_B\rho \mid R(t)\rangle}{\langle \rho \mid \rho\rangle} \\ &= \rho\frac{\langle R(0) \mid R(t)\rangle}{\langle \rho \mid \rho\rangle}\end{aligned} \tag{6.33}$$

Introducing the memory function

$$M_C(\boldsymbol{q},t) = \frac{1}{N}\langle R(\boldsymbol{q},0) \mid R(\boldsymbol{q},t)\rangle \tag{6.34}$$

one derives Eq. (6.33) as

$$\hat{P}O_B R(t) = N\rho(\boldsymbol{q})\frac{M_C(\boldsymbol{q},t)}{\langle \rho(\boldsymbol{q}) \mid \rho(\boldsymbol{q})\rangle} \tag{6.35}$$

The appearance of the factor $\hat{Q}$ implying that both $R(0)$ and $R(t)$ are rapid variables. Inserting the above results to Eq. (6.25), and noticing that $R(\boldsymbol{q},t)$ is orthogonal to $\rho(\boldsymbol{q})$, one obtains

$$\frac{\partial S(q,t)}{\partial t} = -\frac{\omega}{S(q)}S(q,t) + \int_0^t \mathrm{d}t' M_C(\boldsymbol{q},t-t')\frac{S(q,t')}{S(q)} \tag{6.36}$$

Actually, $R(t)$ is equivalent to the stochastic force in Langevin equation, and $M_C(q,t)$ is just the correlation function of this stochastic force, which obviously decays faster than $S(q,t)$. Moreover, since it involves only the rapid part of the variable, $M_C(\boldsymbol{q}, t)$ is mathematically simpler than $S(q,t)$. Usually one first calculates $M_C(q,t)$, and then derives $S(q,t)$ by using Eq. (6.14). At time $t \gg \tau_I$,since $M_C(\boldsymbol{q},t-t')$ decays rapidly for larger $(t-t')$, it is the part of $t \sim t'$ in Eq. (6.36) that contributes most to the integral. Therefore one replaces t' in $S(\boldsymbol{q},t')$ in the integrand by t, expands the integral limit to $[0,\infty]$, and finally derives

$$\begin{aligned}\frac{\partial S(q,t)}{\partial t} &= -\left(\omega(q) - \int_0^\infty \mathrm{d}t' M_C(q,t')\right)\frac{S(q,t)}{S(q)} \\ &\equiv -q^2 D_C^L(q)S(q,t)\end{aligned} \tag{6.37}$$

The formula (6.36) is exactly the same as the phenomenological result Eq. (6.14), meanwhile, one obtains also the microscopic expression for calculating $\omega(\boldsymbol{q})$ and memory function.

In this way, $S(q,t)$ is still of exponential form at long-time, with its slope being the long-time collective diffusion coefficient

$$D_C^L(q) = \frac{1}{S(\boldsymbol{q})}\left(\omega(\boldsymbol{q}) - \int_0^\infty \mathrm{d}t' M_C(q,t')\right)$$

This, however, when $q \to 0$, is the diffusion coefficient D_C under hydrodynamic limit.

The numerical stability of Eq. (6.36) is not good, hence for the convenience of calculation, we introduce the reduced memory function $\tilde{M}'_C(q,s)$

$$\tilde{M}_C(q,s) = q^2 D_0 H(q) \frac{\tilde{M}'_C(q,s)}{1+\tilde{M}'_C(q,s)} \tag{6.38}$$

Accordingly the inverse Laplace transform of Eq. (6.13) becomes

$$\frac{\partial S(q,t)}{\partial t} = -\frac{\omega}{S(q)} S(q,t) - \int_0^t \mathrm{d}t' M'_C(q,t-t') \frac{\partial S(q,t')}{\partial t'} \tag{6.39}$$

which is numerically stable. Usually this formulae is the one to be solved in practice.

Both Eqs. (6.36) and (6.39) are derived through mathematical calculations starting from the continuity equation. Since the continuity equation is strictly valid and no approximations have been introduced during the derivation, Eqs. (6.36) and (6.39) are exact. However, in practice one has to introduce approximations when calculating $M'_C(q,t)$, among which the most commonly used method is mode coupling theory (MCT). In this way, the dynamical calculation of the memory function has been changed to pure static theory by using project operator method and MCT. Once $M'_C(q,t)$ is available, Eq. (6.39) reduces to the nonlinear equation of $S(q,t)$, which can be solved numerically.

One arrives at the single-particle theory by a very similar derivation. The single particle propagator is just the diagonal part of $S(q,t)$, i.e.,

$$G(q,t) = \left\langle \mathrm{e}^{\mathrm{i}\boldsymbol{q}\cdot(\boldsymbol{r}_1(0)-\boldsymbol{r}_1(t))} \right\rangle \tag{6.40}$$

where $\boldsymbol{r}_1(t)$ denotes the position vector of representative particle at time t. The exact memory function is

$$\begin{aligned}\frac{\partial G(q,t)}{\partial t} &= -q^2 D_S^S(q) G(q,t) \\ &\quad - \int_0^t \mathrm{d}t' M'_S(q,t-t') \frac{\partial G(q,t')}{\partial t'}\end{aligned} \tag{6.41}$$

with $M'_S(q,t)$ is reduced memory function of self-diffusion.

7 Diffusion properties

Here we present some theoretical results, the detailed calculation of which can be found in references. The basic theories and methods used are those given in the forgoing sections. The diffusion properties of HS systems and charged-particle suspensions can be calculated by applying MCT. The relation between the single particle propagator $G(q,t)$ and the average of the square of displacement, $W(t)$, is

$$W(t) = -\lim_{q\to 0} \frac{1}{q^2} G(q,t) \tag{7.1}$$

According to the definition of long-time self-diffusion coefficient D_S^L

$$\lim_{q\to 0} W(t) = D_S^L t \tag{7.2}$$

one obtains the value of D_S^L if the quantity of $G(q,t)$ is available.

Figure 6 shows the relation of D_S^L for HS system as a function of the volume fraction ϕ [34]. It is deduced that the long-time self-diffusion coefficient by using MCT becomes 0 at ϕ=0.525, where ideal MCT glass transition takes place. Obviously the theoretical prediction is smaller than the experimental result. A phenomenological modification is realized by rescaling the volume fraction as $\phi \to \phi\ (\phi_g/0.525)$, ϕ_g being the real vitrification density, approximately 0.62. This value, however, can be determined by equating the MCT result with that of Brownian dynamics simulation [32, 33]. Similar methods may be applied to charge-stabilized suspensions, leading to the result not only related with ϕ, but also dependent on the parameters such as the effective charge of particles and the density of salt added into the suspension. Figure 7 shows the result for a salt-free system with charge Z = 500, where the diffusion coefficient changes with the number density ϕ [35].

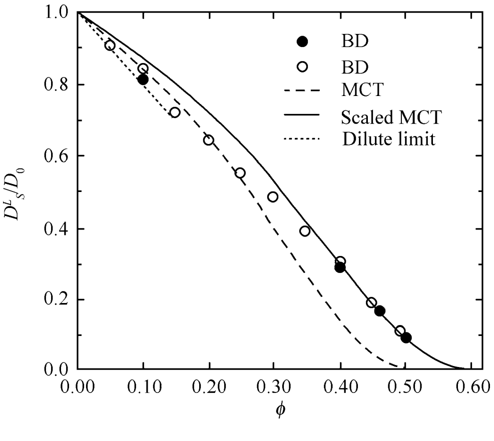

Fig. 6 The function of D_S^L of HS system versus volume fraction ϕ. The open circle [32] and solid circle [33] denote the simulation result from Brownian dynamics. The dashed line represents the long-time self-diffusion coefficient by using MCT, while the solid line represents the result of rescaled MCT. The dotted line represents the result without HI in infinite dilute system, which is $D_S^L/D_0 = 1-2\phi$.

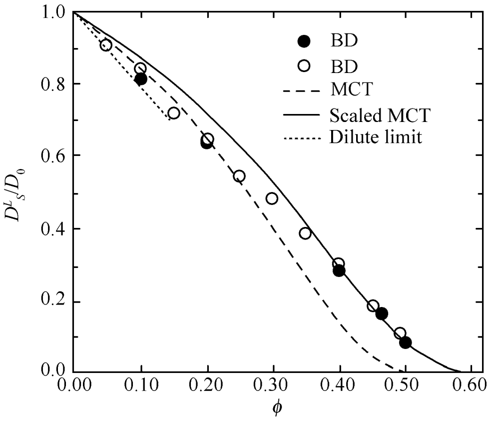

Fig. 7 The results of D_S^L/D_0 for charge-stabilized suspensions by using MCT (with left *y*-axis, solid line) and the peak of the static structure factor $S(q_m)$ by using RMSA (with right *y*-axis, dashed line) versus ϕ. Note that the MCT result relates the dynamic freezing criterion $D_S^L(\phi \approx 0.002\,3)/D_0 \approx 0.1$ with the static freezing criterion. $S(q_m, \phi \approx 0.002\,4) \approx 2.85$. The parameters of the system are: L_B=7.14, the diameter of particle σ=100 nm, and the effective charge Z=500 (with unit *e*).

Now we investigate the change of self-diffusion coefficient from the short-time one, D_S^S, to the long-time one, D_S^L. This result is given by the self-diffusion function $D_S(t)=W(t)/t$, being D_S^S at $t \to 0$, and D_S^L at $t \to \infty$. Figure 8 shows the relation of $W(t)/D_0t$ changing with time [35]. It can be seen that the asymptotic behavior of D_S^L takes place at time $t > 10^{-2}$s.

The collective diffusion is related with the process of the density fluctuation tending to equilibrium (i.e., relaxation), which is described by the dynamic structure factor $S(q,t)$. For charge-stabilized system, Fig. 9 shows the result of $S(q, t)$ by means of various approaches: MCT, Brownian dynamics simulation (BD) [36] and the one through $M_C\,(q, t)$ obtained by the simple exponential decaying method (SEXP) [37].

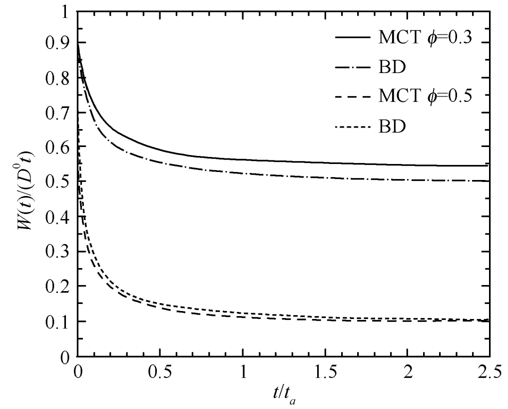

Fig. 8 The results of $W(t)/D_0t$ for HS system changing with reduced time t/t_a. The solid line and the long-dashed line denote the MCT results for volume fraction ϕ=0.3 and ϕ=0.5, respectively; while the dashed line and dotted line represent the BD simulation results corresponding to these two situations [32]. Here $t_a=a^2/D^0$ is the time taken for an isolated spherical particle of radius *a* to diffuse a distance *a*.

The relaxation factor is different on different time scales, where Figs. 10 and 11 [35] present the results obtained by MCT, BD and experiments, corresponding to two wave numbers, respectively, one to the peak q_m of $S(\boldsymbol{q})$, the other to $q=0.87q_m$ [38]. It is seen that $S(q,t)$ corresponding to q_m approaches equilibrium slower; while both curves are not of simple exponential form.

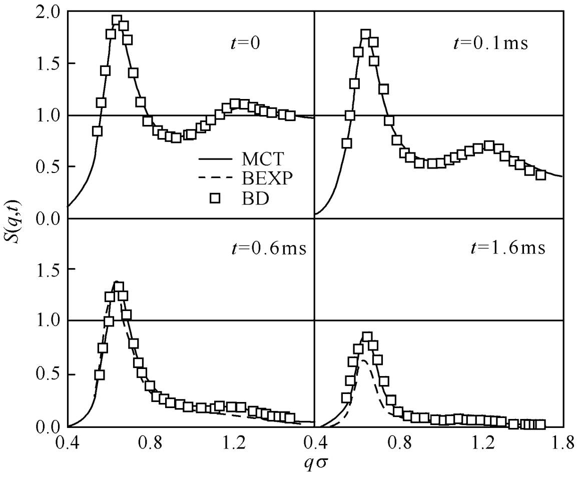

Fig. 9 The results of $S(q,t)$ obtained by means of various methods: MCT (denoted by solid line), Brownian dynamics simulation (BD, represented by open square) [36], and the results calculated through $M_C(q,t)$ by simple exponential decay (SEXP, denoted by dashed line) [37]. The parameters of the system are: the diameter of particles σ=46 nm, volume fraction $\phi=0.44\times10^{-3}$, $\kappa\sigma$=0.25, and $D_0=9.5\times10^{-12}$m²/s.

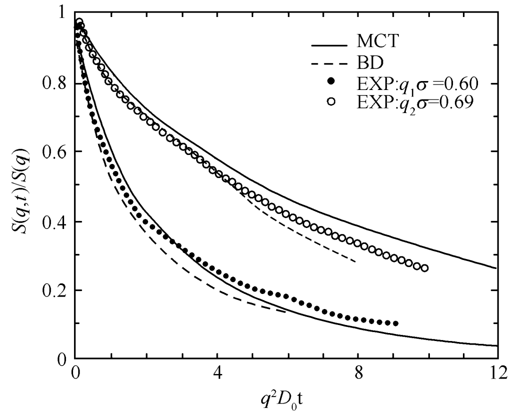

Fig.10 The relation of normalized dynamic structure factor of charge-stabilized suspensions changing with the reduced time q^2D^0t. Two curves correspond to two situations with wavenumber $q_1\sigma$=0.60 and $q_2\sigma \approx q_m\sigma$=0.69, respectively, where the solid line represents the MCT result, and the dashed line denotes the result from Brownian dynamic simulation (BD). The filled circle and the open circle represent experimental results corresponding to these two situations [38].

We point out that all MCT results presented here are those without hydrodynamic interaction. However, many-body HI should be taken into account in those HS systems with high number densities of particles. This, accordingly, leads to the results comparable with those of experiments. Since this is a very difficult problem, only few approximative theories are available. Medina-Noyold [39] and Brady [40] suggested a semi-empirical rescaling method, which presumes that the long-time contribution to the transport coefficients, i.e., the memory effect, is caused by configuration relaxation ignorant of HI. On the contrary, in the short-time part, HI is taken into account. In this way, the transport coefficient can be decomposed to the short-time part with HI and the MCT result of configurational contribution. For the self-diffusion case,

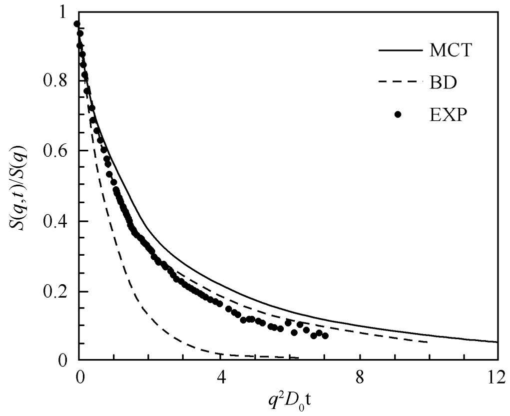

Fig.11 The relation of normalized dynamic structure factor of charge-stabilized suspensions changing with the reduced time q^2D^0t, for wavenumber $q_3\sigma=1.47$. The solid line denotes the MCT result, the dashed line represents the results of Brownian dynamic simulation (BD), while the filled circle is the corresponding experimental results [38]. In addition, the dotted line denotes the short-time decay of $S(q_3,t)$, which is $\exp[-q^2D_0t]$.

$$D_S^L = \frac{D_S^S}{D_0} D_S^{L,MCT} \tag{7.3}$$

where the first factor is obtained by semi-empirical rescaling method as [41]

$$\frac{D_S^S}{D_0} = (1-1.56\phi)(1-0.27\phi) \tag{7.4}$$

For the case of very small particle number density, the expression reduces to the previous one, $D_S^S/D_0 = 1-1.83\phi$, leading to $D_S^S = 0$ for $\phi = 0.64$, i.e., the case of random close packing. These results are presented in Fig. 12 [35]. It is shown that rescaling influences the results greatly, which makes the theoretical result conform to the experimental one. Similarly, rescaling method can also be applied to calculate the long-time collective diffusion coefficient.

Finally, we discuss a little about the weak coupling approximation (WCA) and the long-time tail. When HI is ignored, both $M_C(q,t)$ and $M_S(q,t)$ can be calculated under WCA limit. For dilute systems with weak interactions, one may expand the memory function according to the potential energy $U(\boldsymbol{r}^N)$. It is termed as WCA when only the first term is included.

Applying the discussions to the self-diffusion case, we consider the asymptotic behavior of the memory function $M_S(q,t)$ at long time $t \gg \tau_I$. Take the dilute Yukawa system with weak repulsive interaction as an example, with the interaction potential [44]

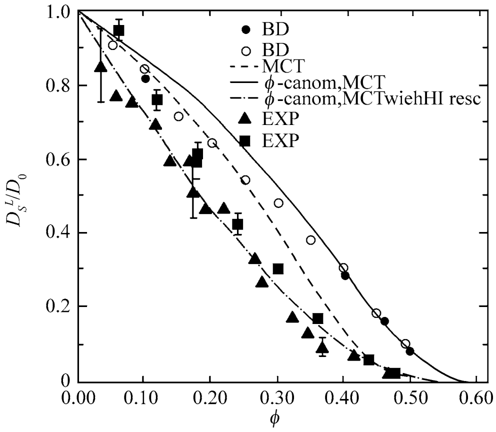

Fig.12 The relation of D_S^L in HS systems changing with the volume fraction ϕ. The filled circle [32] and the open circle [33] denote the results obtained from Brownian dynamics simulation (BD). The dashed line represents the long-time self-diffusion coefficient by using MCT without renormalization by ϕ and without scaling by HI; while the dashed line denote the results by using MCT with renormalization by ϕ and with scaling by HI. The filled triangle [42] and filled square [42] are the corresponding experimental results.

$$\beta u(r) = A\frac{e^{-\kappa r}}{r} \tag{7.5}$$

here κ is the inverse of the screening length, and A has the dimension of length. Through some calculations, we obtain

$$W(t) \approx D_S^L t + W_0 - \frac{A\tau_I}{12}(2t/\tau_I)^{-1/2} \tag{7.6}$$

where the long-time tail is due to the collective retardation effect of the motion of particles around the representative particle.

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