Brownian motion of two interacting particles under a square-well potential

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The Smoluchowski equation for the Brownian motion of two interacting particles through a square-well potential whose heights are infinitely large at the origin and finite at the other positions of u (>0) is solved exactly for the Laplace transform of the conditional density with respect to time t. The analytical expression for the distinct part of the dynamic structure factor at the initial time with the δ function has been also obtained exactly. Moreover, we have calculated the asymptotic behavior of the mean-square displacement expressed as an explicit function of t and found that it is a function of the height of the potential at u, which directly indicates a deviation from the Einstein relation.

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I. INTRODUCTION

Although classical theory of Brownian motion describing time evolution of particles as a function of space coordinates has been established a long time ago [1], exact solutions for equations of Smoluchowski and Fokker-Planck-Kramers have been obtained only for limited numbers of extremely simple cases such as free and bound motions under the harmonic potential. This is a clear contrast to equilibrium statistical mechanics where various kinds of molecular interactions are allowed to be interpreted [2]. In the mean time, recent experimental techniques enable us to measure various dynamic processes of molecules in liquids or in solutions, that require detailed theoretical information on the molecular interaction to interpret their results satisfactorily [3]. It is, therefore, rather acute to work out significant unsolved problems in the field. A step to be taken is to consider that an attractive interaction of two molecules in fluids will be the square-well potential, if we go further than the presently solved case of repulsive interaction by the hard-sphere potential [4]. Our future aim is to treat N interacting particles in the long-time region where a system we are concerned with is near equilibrium. When we investigate the long-time dynamic process by the molecular dynamics, we need a very long computing time. So, we are to use a self-consistent-field (SCF) procedure described later based on the Smoluchowski equation and to examine the N particle system analytically. If it is difficult, we are to use a numerical technique that will be much more efficient than the molecular dynamics. To this end, we need a basis solution of two-particle system, just like the case where the solution for the hydrogen atom is indispensable for investigating many electron systems by the SCF procedure.

It will be shown that we will be able to find the exact expression of the conditional density for the square-well potential and work out the distinct dynamic structure factor responsible for elastic neutron scattering analytically based on the Smoluchowski equation. In addition, we will investigate the mean-square displacement as a function of time and the potential height to see how the attractive interaction delays the diffusion and how it deviates from the Einstein relation which is believed to hold for most fluids.

II. ONE-DIMENSIONAL MOTION

To consider Brownian motion of particles in a fluid, we start with the following Smoluchowski equation for the conditional density $\rho(x,\tau)$ expressed as a function of time τ and the position x:

$$\frac{\partial\rho(x,\tau)}{\partial\tau}=D\frac{\partial}{\partial x}\left[\frac{\partial\rho(x,\tau)}{\partial x}-\frac{f(x)}{k_BT}\rho(x,\tau)\right], \quad (1)$$

where D is the diffusion constant, $f(x)$ is the external force, k_B is the Boltzmann constant, and T is the temperature. We shall introduce the reflecting boundary (infinitively high potential) at $x=0$ and the square-well potential $V(x)$ with finite height at $x=u$ as shown in Fig. 1. These are expressed by

$$J(x,\tau)=-D\left[\frac{\partial\rho(x,\tau)}{\partial x}-\frac{f(x)}{k_BT}\rho(x,\tau)\right]=0 \quad (x=0)$$

$$V(x)=-V_0 \quad (0<x<u) \quad (2)$$

$$V(x)=0 \quad (x>u) .$$

where $J(x,\tau)$ is the flux. From the relation,

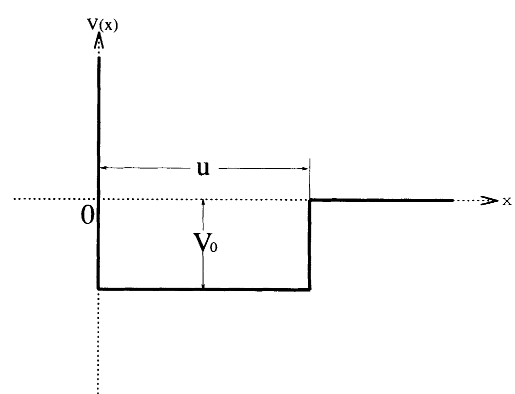

FIG. 1. Square-well potential $V(x)$.

$$f(x)=-\frac{dV(x)}{dx} \tag{3}$$

we see that

$$f(x)=-V_0\delta(x-u) . \tag{4}$$

Thus, our problem is to find the solution of the following equation with the boundary conditions in Eq. (2):

$$\frac{\partial\rho(x,t)}{\partial t}=\frac{\partial}{\partial x}\left[\frac{\partial\rho(x,t)}{\partial x}+A\delta(x-u)\rho(x,t)\right] \tag{5}$$

and the initial condition,

$$\rho(x,0)=\delta(x-x_0) \quad \text{at } t=0 , \tag{6}$$

where

$$t=D\tau \quad \text{and} \quad A=\frac{V_0}{k_BT} . \tag{7}$$

A convenient way to treat the square-well potential may be to use an integral transform because of the presence of the δ function which has the clear meaning only after being integrated. To this end, we introduce the double Laplace transform by the following relations:

$$\phi(x,\lambda)=L[\rho(x,t)]=\int_0^\infty \rho(x,t)e^{-\lambda^2 t}dt , \tag{8}$$

$$\Phi(\xi,\lambda)=\int_0^\infty \phi(x,\lambda)e^{-\xi x}dx . \tag{9}$$

On taking the Laplace transforms on both sides of Eq. (5) and using Eqs. (2) and (6), we find that

$$(\xi^2-\lambda^2)\Phi(\xi,\lambda)=-e^{-\xi x_0}+\xi\phi(0,\lambda)-A\phi(u,\lambda)\xi e^{-\xi u} . \tag{10}$$

The inverse Laplace transform with respect to ξ leads to

$$\phi(x,\lambda)=-\frac{1}{\lambda}H(x-x_0)\sinh[\lambda(x-x_0)] - AH(x-u)\phi(u,\lambda)\cosh[\lambda(x-u)] + \phi(0,\lambda)\cosh(\lambda x) , \tag{11}$$

where $H(x)$ is the Heaviside unit function that is 0 for $z<0$ and 1 for $x>0$. To avoid divergence at $x\to\infty$, we have to set

$$\phi(0,\lambda)-A\phi(u,\lambda)e^{-\lambda x_0}=0 , \tag{12}$$

which leads to

$$\phi(x,\lambda)=\frac{1}{2\lambda}e^{-\lambda(x-x_0)}-\frac{A}{2}\phi(u,\lambda)e^{-\lambda(x-u)} + \frac{\phi(0,\lambda)}{2}e^{-\lambda x} \quad [x\ge \max(u,x_0)] . \tag{13}$$

From now on, we shall assume that

$$u>x_0 . \tag{14}$$

On putting $x=u$ in Eq. (13), we have another condition,

$$(2+A)\phi(u,\lambda)=\frac{1}{\lambda}e^{-\lambda(u-x_0)}+\phi(0,\lambda)e^{-\lambda u} . \tag{15}$$

Therefore, it follows from (12) and (14) that

$$\phi(0,\lambda)=\frac{1}{\lambda}e^{-\lambda x_0}+\frac{2A}{\lambda}\frac{\cosh(\lambda x_0)}{(A+2)e^{2\lambda u}-A} \tag{16}$$

and

$$\phi(u,\lambda)=\frac{2}{\lambda}\frac{e^{\lambda u}\cosh(\lambda x_0)}{(A+2)e^{2\lambda u}-A} . \tag{17}$$

We, therefore, find the following result:

$$\phi(x,\lambda)=-\frac{1}{\lambda}H(x-x_0)\sinh[\lambda(x-x_0)]+\frac{1}{\lambda}e^{-\lambda x_0}\cosh(\lambda x)+\frac{A}{\lambda}\cosh(\lambda x_0)\frac{[1-H(x-u)]e^{\lambda x}+[1-H(x-u)e^{2\lambda u}]e^{-\lambda x}}{(A+2)e^{2\lambda u}-A} . \tag{18}$$

The number of particles within the square well can be readily calculated from (18) and we find

$$L[N_b(t)]=\int_0^u \phi(x,\lambda)dx=\frac{1}{\lambda^2}-\frac{2}{\lambda^2}\frac{e^{-\lambda u}\cosh(\lambda x_0)}{2+A-Ae^{-2\lambda u}} . \tag{19}$$

Whereas, the mean-square displacement, $\langle x^2\rangle$ is given by

$$L[\langle x^2\rangle]=\frac{x_0^2}{\lambda^2}+\frac{2}{\lambda^4}-\frac{4}{\lambda^4}\lambda u\frac{Ae^{-\lambda u}\cosh(\lambda x_0)}{2+A-Ae^{-2\lambda u}} . \tag{20}$$

III. THREE-DIMENSIONAL MOTION UNDER SPHERICALLY SYMMETRIC SQUARE-WELL POTENTIAL

Let us now consider the case of three-dimensional Brownian motion under the spherically symmetric square-well potential whose radial position is denoted by r where the Smoluchowski equation is given by

$$\frac{\partial\rho(r,t)}{\partial t}=\frac{1}{r^2}\frac{\partial}{\partial r}r^2\left[\frac{\partial\rho(r,t)}{\partial r}-\frac{f(r)}{k_BT}\rho(r,t)\right] , \tag{21}$$

which leads to

$$\frac{\partial\rho(r,t)}{\partial t}=\frac{1}{r^2}\frac{\partial}{\partial r}r^2\left[\frac{\partial\rho(r,t)}{\partial r}+A\delta(r-u)\rho(r,t)\right] . \tag{22}$$

The initial condition this time is

$$\rho(r,0)=\frac{\delta(r-r_0)}{r^2} \quad \text{at } t=0 . \tag{23}$$

The definition in Eq. (8) is still valid, if x is replaced by r, but Eq. (9) is not convenient. So, on taking into account the spherical symmetry, we employ the following Hankel transform:

$$Q(\xi,\lambda)=\int_0^\infty \phi(r,\lambda)j_0(\xi r)r^2 dr \ , \tag{24}$$

where $j_0(z)$ is one of spherical Bessel functions which are

$$j_0(z)=\sin z/z, \quad j_1(z)=(\sin z - z\cos z)/z^2, \ldots .$$

On taking the inverse transform, we see that

$$r\phi(r,\lambda)=\frac{2}{\pi}\int_0^\infty [\xi Q(\xi,\lambda)]\sin\xi r \, d\xi \ , \tag{25}$$

which is the Fourier sine transform. The idea to use this integral transform is based on the following relation so that the Laplacian in Eq. (22) can be conveniently expressed:

$$\frac{d^2 j_0(z)}{dz^2}+\frac{2}{z}\frac{dj_0(z)}{dx}=-j_0(z) \ , \tag{26}$$

which enables us to transform Eq. (22) into

$$Q(\xi,\lambda)=\frac{j_0(\xi r_0)}{\xi^2+\lambda^2}+[Au^2\phi(u,\lambda)]\frac{\xi j_1(\xi u)}{\xi^2+\lambda^2} \ , \tag{27}$$

where we have used the following boundary conditions:

$$J(r,t)=-D\left[\frac{\partial \rho(r,t)}{\partial r}+A\delta(r-r_0)\rho(r,t)\right]=0 \quad \text{at } r=0,$$

and

$$\lim_{\sigma\to 0}\sigma^3\rho(\sigma,t)=0 \ . \tag{28}$$

In view of Eqs. (25) and (27), on taking the inverse Fourier transform we find that

$$\phi(r,\lambda)=\frac{1}{rr_0}\times\begin{Bmatrix}\frac{1}{\lambda}e^{-\lambda r_0}\sinh(\lambda r), & (0<r<r_0)\\ \frac{1}{\lambda}e^{-\lambda r}\sinh(\lambda r_0), & (r_0<r<\infty)\end{Bmatrix}+Au\phi(u,\lambda)\frac{1}{r}\times\begin{Bmatrix}\left[\frac{1}{\lambda u}+1\right]e^{-\lambda u}\sinh(\lambda r) & (0<r<u)\\ \left[\frac{1}{\lambda u}-1\right]e^{-\lambda r}\sinh(\lambda u) & (u<r<\infty) \ .\end{Bmatrix} \tag{29}$$

We now determine $\phi(u,\lambda)$ by putting $r=u$ in Eq. (29) and deduce that

$$\phi(u,\lambda)=\frac{1}{u}p(\lambda,u) \ , \tag{30}$$

where

$$p(\lambda,u)=\frac{\sinh(\lambda r_0)}{\lambda r_0}\frac{1}{e^{\lambda u}+A\left[\cosh(\lambda u)-\frac{\sinh(\lambda u)}{\lambda u}\right]} \ . \tag{31}$$

The number of particles inside the potential, $N_b(t)$ can be obtained from the relation

$$L[N_b(t)]=\frac{1}{\lambda^2}-\frac{\lambda u+1}{\lambda^2}p(\lambda,u) \ . \tag{32}$$

The mean square displacement satisfies the following relation:

$$L[\langle r^2(t)\rangle]=\frac{r_0^2}{\lambda^2}+\frac{6}{\lambda^4}-2\frac{Au^2}{\lambda^2}p(\lambda,u) \ . \tag{33}$$

IV. DISCUSSION

We shall investigate the long-time asymptotic expressions of the mean-square displacements of the one- and three-dimensional motions in Eqs. (20) and (33), respectively. In view of the fact that the initial values must vanish as time goes on, the long-time behavior in which we are interested should not depend on the choice of the initial condition. Hence it is useful to calculate the mean-square displacement for the uniform distribution at $t=0$ in $0<x_0<u$ and $0<r_0<u$, where Eqs. (20) and (33) must be integrated over x_0 and r_0, respectively. Equation (20) after taking average of x_0 leads to

$$L[\langle x^2\rangle]=\frac{u^2}{3\lambda^2}+\frac{2}{\lambda^4}-\frac{2}{\lambda^4}\frac{A\sinh(\lambda u)}{e^{-\lambda u}+A\sinh(\lambda u)} \ . \tag{34}$$

Now, we shall concentrate on finding the long-time behavior of the following formula:

$$\Psi(\lambda)=\frac{A}{\lambda^4}\frac{\sinh(\lambda u)}{e^{-\lambda u}+A\sinh(\lambda u)}=\frac{A}{\lambda^4}\frac{1}{A+1+\coth(\lambda u)}$$
$$=\frac{A}{\lambda^4}\sum_{n=0}^{\infty}\frac{(-1)^n\coth^n(\lambda u)}{(A+1)^{n+1}} \ . \tag{35}$$

To this end, we note that

$$\coth z=\frac{1}{z}+2z\sum_{n=1}^{\infty}\frac{1}{z^2+n^2\pi^2} \tag{36}$$

and

$$L^{-1}\left[\frac{1}{\lambda^{2\mu+1}}\frac{1}{(\lambda^2+a)^\nu}\right]=\frac{t^{\nu+\mu-1/2}}{\Gamma(\nu)\Gamma(\mu+\frac{1}{2})}\times\int_0^1 e^{-aty}y^{\nu-1}(1-y)^{\mu-1/2}dy \quad (\text{for } a>0) \tag{37}$$

(see Ref. [5] on p. 238, after expressing the confluent hypergeometric function by integral representation). In view of Eq. (36), we see that $\coth^n(\lambda u)$ after decomposing into partial fractions can be expressed by the summation of the terms in the form given on the left hand side of Eq. (37) in the square brackets. In addition, for a large value of t, the significant contributions to the integral on the right-hand side of Eq. (37) arise from function near $y \ll 1$ in the integrand in view of the Laplace method in asymptotic expansion, which enables us to replace the upper limit in the integral to ∞. Thus, we obtain an asymptotic expression for the left-hand side in Eq. (37),

$$L^{-1}\left[\frac{1}{\lambda^{2\mu+1}}\frac{1}{(\lambda^2+a)^\nu}\right] \approx \frac{1}{\Gamma(\mu+\frac{1}{2})}\frac{t^{\mu-1/2}}{a^\nu}{}_2F_0\left[\nu,\tfrac{1}{2}-\mu;\frac{1}{at}\right], \quad (38)$$

where ${}_2F_0(a,b;z)$ is a hypergeometric function. Note that the highest order in t in Eq. (38) is $t^{\mu-1/2}$. Since the full asymptotic expression for $L^{-1}[\Psi(\lambda)]$ seems difficult, we have carried out our calculations only for $n=1$ and 2, which leads to

$$\langle x^2(t)\rangle = \frac{u^2}{3}+2\left[\frac{1}{(A+1)}t+\frac{A}{(A+1)^2}\left[\frac{4}{3u\sqrt{\pi}}t^{3/2}+\frac{2u\sqrt{t}}{3\sqrt{\pi}}+O(t^{-1/2})\right]-\frac{A}{(A+1)^3}\left[\frac{t^2}{2u^2}+\tfrac{2}{3}t+O(1)\right]\right]. \quad (39)$$

If we collect the proportional coefficients for t to see how the Einstein relation looks like for the present case, we see that

$$\langle x^2(t)\rangle = \frac{u^2}{3}+2\left[\frac{1}{A+1}-\frac{2A}{3(A+1)^3}\right]t. \quad (40)$$

It is beyond doubt that Eqs. (39) and (40) are valid for large values of A, even though they happen to give the correct Einstein relation in the case of $A=0$. We emphasize that coefficients obtained after expanding $\Psi(\lambda)$ of Eq. (35) with respect to A^{-1} instead of $(A+1)^{-1}$ become divergent except the first term when the inverse Laplace transform is taken. Now, let us consider the long-time behavior for the three-dimensional case. We assume that the initial distribution of the particles is uniform within the well, which requires to average Eq. (33) over r_0, namely,

$$\frac{3}{u^3}\int_0^u \frac{\sinh(\lambda r_0)}{\lambda r_0}r_0^2 dr_0 = \frac{3}{\lambda^2u^2}\left[\cosh(\lambda u)-\frac{1}{\lambda u}\sinh(\lambda u)\right], \quad (41)$$

which leads to

$$L[\langle r^2(t)\rangle] = \frac{3u^2}{5\lambda^2}+\frac{6}{\lambda^4}-\mu(\lambda), \quad (42)$$

where

$$\mu(\lambda) = \frac{6A}{\lambda^4}\frac{1}{A+1+\gamma(\lambda)} = \frac{6A}{\lambda^4}\sum_{n=1}^{\infty}\frac{[-\gamma(\lambda)]^n}{(A+1)^{n+1}} \quad (43)$$

whose long-time asymptotic expression we wish to obtain. In Eq. (43) we have defined $\gamma(\lambda)$ by the relation,

$$\gamma(\lambda) = \frac{(\lambda u+1)\sinh(\lambda u)}{\lambda u\cosh(\lambda u)-\sinh(\lambda u)}. \quad (44)$$

It is extremely important to express $\gamma(\lambda)$ by the relation,

$$\gamma(\lambda) = \left[1+\frac{1}{\lambda u}\right]\frac{I_{1/2}(\lambda u)}{I_{3/2}(\lambda u)}. \quad (45)$$

Further, we note the identity

$$\frac{I_{1/2}(iy)}{I_{3/2}(iy)} = -i\frac{J_{1/2}(y)}{J_{3/2}(y)}. \quad (46)$$

Since $J_{3/2}(y)$ has simple roots at r_n, where $n=1,2,3,\ldots$, except at $y=0$, we can express the second term on the right-term side of Eq. (45) similarly to Eq. (36) and find that

$$\frac{I_{1/2}(z)}{I_{3/2}(z)} = \frac{3}{z}+2z\sum_{n=1}^{\infty}\frac{1}{z^2+r_n^2}. \quad (47)$$

Thus, we can use relations in Eqs. (37) and (38) to get the asymptotic expression as before. By carrying out the terms in Eq. (43) up to $n=1$ this time, we deduce that

$$\langle r^2(t)\rangle = \frac{3u^2}{5}+6\left[\frac{1}{A+1}t+\frac{A}{(A+1)^2}\left[\frac{3t^2}{2u^2}+\frac{4}{u\sqrt{\pi}}t^{3/2}+\frac{t}{5}+\frac{2ut^{1/2}}{5\sqrt{\pi}}+O(1)\right]\right]. \quad (48)$$

If we keep the t term, we see that

$$\langle r^2(t)\rangle = \frac{3u^2}{5}+6\left[\frac{1}{A+1}+\frac{A}{5(A+1)^2}\right]t. \quad (49)$$

This explicitly appears like the result in Eq. (40) that the mean-square displacement deviates significantly from the Einstein relation when A becomes large (see Fig. 2). The attractive potential drags the diffusion of particles from the square well. Even though this point is neglected mostly in the literature, it should be pointed out that the determination of the diffusion constant from the plot of

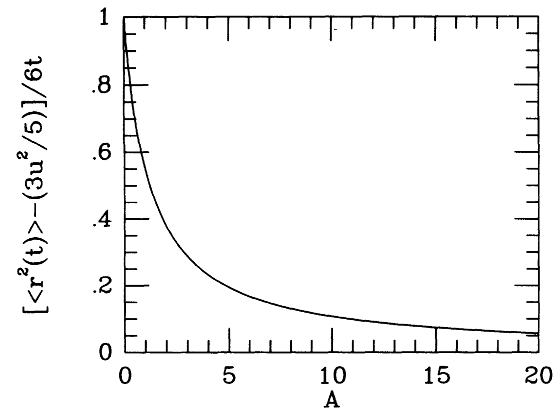

FIG. 2. Plot $[\langle r^2(t)\rangle-(3u^2/5)]/6t$ vs A.

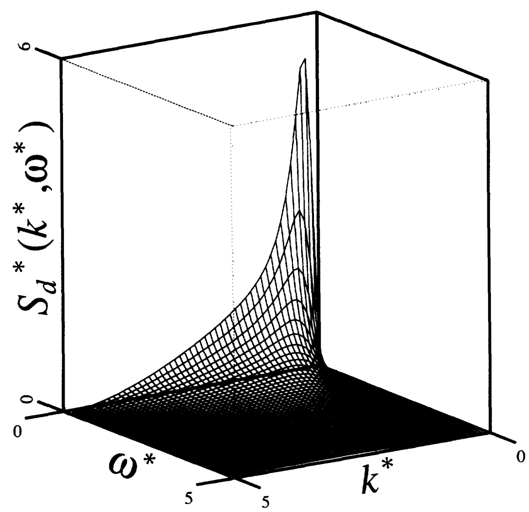

FIG. 3. Three-dimensional plot of $S_d^*(k^*,\omega^*)$ as a function of k^* and ω^*.

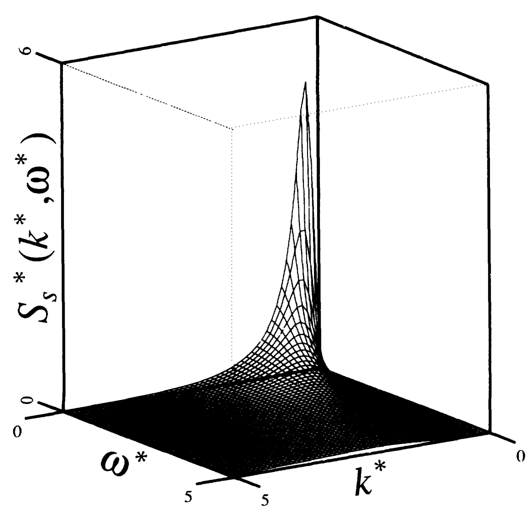

FIG. 4. Three-dimensional plot of $S_s^*(k^*,\omega^*)$ obtained from the Gaussian distribution as a function of k^* and ω^*.

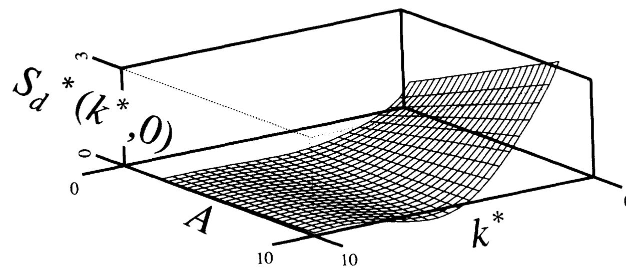

FIG. 5. Three-dimensional plot of $S_d^*(k^*,0)$ as a function of k^* and A.

the slope of the mean-square displacement vs times is not totally flawless. In fact, there is experimental evidence which shows the deviation [6]. By treating Brownian motion under the logarithmic potential, Morita also observed the significant difference [7].

From the definitions in Eqs. (8) and (24), on replacing ξ and λ^2 by ik and $i\omega$, respectively, where k and ω are wave number and angular frequency, respectively, we readily identify the real part of the complex $Q(ik,\sqrt{i\lambda})/\pi$ in Eq. (27) with the distinct part of the dynamic structure factor usually denoted by $S_d(k,\omega)$. Because the expression in Eq. (27) is exact, it may be worthwhile plotting $S_d^*(k^*,\omega^*)$, where $S_d^*=S_d(k,\omega)/\ u^{2,}$ $k^*=ku$ and $\omega^*=\omega u^2/D$. The result is shown in Fig. 3 for $A=10.0$ and $r_0=0.0$, which means that for $t<0$ two particles have been at the same position sticking together (for example, an ion pair) and suddenly at $t=0$ they are subject to the Brownian movement under the square-well potential. This should be compared with the self part of dynamic factor obtained from the Gaussian distribution in Fig. 4. We see significant differences particularly for small ω^*, where an oscillatory behavior shown up. To see these oscillations more clearly, we have plotted $S_d^*(k^*,0)$ as a function of A and k^* in Fig. 5 from which it is evident that the larger A becomes, the stronger the amplitude of the oscillation is. Regarding this $S_d^*(k^*,0)$ as the maximum value, we have also obtained the half width $\Delta\omega^*$ of the half height of $S_d^*(k^*,0)$ and have shown it in Fig. 6 where we can see that the oscillatory behavior is pronounced for small A.

In order to emphasize the significance of the present paper further, let us consider N particle system described by the following Smoluchowski equation:

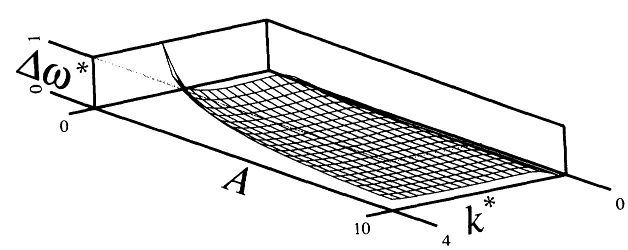

FIG. 6. Three-dimensional plot of the half-width $\Delta\omega^*$ as a function of k^* and A.

$$\frac{\partial\rho(X_1,X_2,\ldots,X_N,t)}{\partial t}=\sum_{i=1}^{N}\left\{\frac{\partial}{\partial X_i}\left[\frac{\partial\rho(X_1,X_2,\ldots,X_N,t)}{\partial X_i}-\frac{1}{k_BT}\sum_{j\neq i}^{N}f_{ij}(X_1,X_2,\ldots,X_N)\times\rho(X_1,X_2,\ldots,X_n,t)\right]\right\}, \tag{50}$$

where X_i represents the position of particle i in one dimension for brevity and f_{ij} is the force acting on particle i from the surrounding particles j. On assuming

$$\sum_{j\neq i}^{N} f_{ij}(X_1,X_2,\ldots,X_N) \approx \sum_{j\neq i}^{N}\int\int\cdots\int f_{ij}(X_1,X_2,\ldots,X_N)\rho(X_1,t)\rho(X_2,t),\ldots,\rho(X_N,t)dX_1dX_2\cdots dX_N=F(X_i,t) \tag{51}$$

we find

$$\frac{\partial\rho(X_i,t)}{\partial t}=\frac{\partial}{\partial X_i}\left[\frac{\partial\rho(X_i,t)}{\partial X_i}-\frac{1}{k_BT}F(X_i,t)\rho(X_i,t)\right], \tag{52}$$

which can be solved by the self-consistent field method, where the value of $\rho(X_i,t)$ can be improved successively. We see that the solution of the present study will be useful for setting up $\rho(X_i,t)$ as the first trial function.

ACKNOWLEDGMENT

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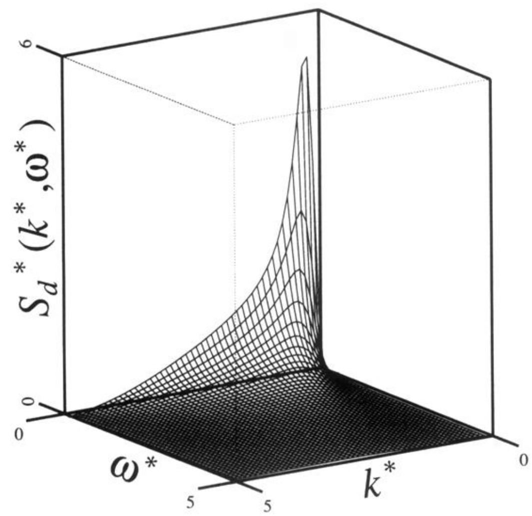

FIG. 3. Three-dimensional plot of $S_d^*(k^*,\omega^*)$ as a function of k^* and ω^*.

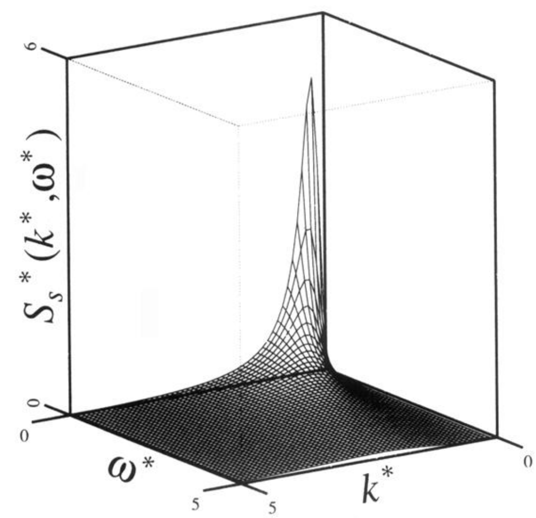

FIG. 4. Three-dimensional plot of $S_s^*(k^*,\omega^*)$ obtained from the Gaussian distribution as a function of k^* and ω^*.