Long-range interaction between Brownian particles

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The interaction potential for Brownian particles is computed in the limit of large interparticle separation. It is shown that the particles repel each other with a force that is inversely proportional to the cube of the separation. The interaction between Brownian particles and a plane wall is also considered.

As is well known, the theory, developed by Lifshitz, Dzyaloshinskiĭ, and other researchers,[1-3] of the long-range dispersion interaction between macroscopic bodies allows us to consider the interaction between objects in a medium. In particular, it allowed the solution of the problem of the interaction of small particles located at large distances from each other in a fluid. Here, in contrast to the problem in a vacuum, there also obtains the specific interaction mechanism connected with the exchange of phonons across a medium. The medium in this case is considered to be compressible and inviscid. In such a treatment the interaction disappears in the limit when the medium and the particles can be considered to be incompressible.

In the present paper we show that, even in this case, if we allow for the viscosity and the fact that the particles in the fluid are not stationary but execute Brownian motion, then there arises between the particles an interaction that is weak, but relatively slowly decreases with distance. The physical essence of this interaction is the following: when a particle moves, it induces motion in the surrounding fluid layers, which, in turn, is capable of acting on the neighboring particles and setting them in motion.[4] It would appear that, on the average, this motion, like Brownian motion, does not have a preferred direction. But this is not so. As will be shown below, the relative displacement of the particles is characterized by a definite regular, besides a random, part. In other words, the consistent particle motions are such as would occur if there acted between the particles entirely determinate forces that in the general case depend on the distance and the particle shape. Allowance for these forces can be of interest only when no other interaction mechanisms exist. For example, it is of interest to take into consideration the interaction between macromolecules dissolved in water in the absence of interactions of the electrical nature.

Let us assume that the Reynolds number $\mathrm{Re} = vl\rho/\eta \ll 1$ (where v and l are the characteristic values of the particle velocity and particle separation; ρ and η are the density and viscosity of the fluid). The velocity field produced by a spherical particle of radius R_1 moving with velocity v_0 is described in this case by the Stokes solution[5]:

$$\mathbf{v}'(\mathbf{r}) = [(3R_1/r' + R_1^3/r'^3)\mathbf{v}_0 + [3R_1(\mathbf{v}_0\mathbf{r}')/r'](1 - R_1^2/r'^2)\mathbf{r}']/4$$
$$\approx (3R_1/4)[\mathbf{v}_0/r' + (\mathbf{v}_0\mathbf{r}')\mathbf{r}'/r'^3], \quad r' \sim l \gg R_1 \tag{1}$$

(where $\mathbf{r}' = \mathbf{r} - \mathbf{r}_1$, where $\mathbf{r}_1$ is the radius vector specifying the position of the center of the first particle). Now let there be located at the point $\mathbf{r} = \mathbf{r}_2$ the center of a second spherical particle of radius R_2. We shall, for simplicity, assume that the second particle is stationary (this assumption has no effect on the final result). Since the fluid at the location of the second particle moves the velocity $\mathbf{v}'(\mathbf{r} = \mathbf{r}_2)$, there occurs around it a velocity self-field $\mathbf{v}''(\mathbf{r})$. As a result, the fluid at the location of the first particle acquires an additional velocity $\mathbf{v}''(\mathbf{r}_1)$, which produces a force $\mathbf{f}$ equal to $6\pi R_1\eta\mathbf{v}''(\mathbf{r}_1)$:

$$\mathbf{f}(\mathbf{r}_1;\ \mathbf{r}_2;\ \mathbf{v}_0) \approx -6\pi R_1\eta(9R_1R_2/16)[\mathbf{v}_0/|\mathbf{r}_1-\mathbf{r}_2|^2$$
$$+3(\mathbf{v}_0(\mathbf{r}_1-\mathbf{r}_2))(\mathbf{r}_1-\mathbf{r}_2)/|\mathbf{r}_1-\mathbf{r}_2|^4]. \tag{2}$$

The formula (2) does not take account of the interaction's retardation, which is determined by the time τ_1 required for the establishment of the Stokes velocity distribution in the region between the particles. The quantity τ_1 is, in order of magnitude, equal to $|\mathbf{r}_1 - \mathbf{r}_2|^2\rho/\eta$. Therefore, the correct treatment requires that we take the velocity $\mathbf{v}_0$ entering into (2) to be not the true velocity of the particle at the given moment of time, but the velocity averaged over time intervals of the order of τ_1; then the force $\mathbf{f}$ also has the meaning of an averaged force.

In order to determine the regular part of the force acting on a particle, we should average (2) over all possible $\mathbf{v}_0$. This is equivalent to averaging over time intervals $\tau' \gg \tau_1$. In this case the condition $\tau' \ll \tau_2$, where τ_2 is the time during which the Brownian particle diffuses over a distance of the order of $|\mathbf{r}_2 - \mathbf{r}_1|$, should be fulfilled. In order of magnitude, the quantity $\tau_2 = |\mathbf{r}_1 - \mathbf{r}_2|^2R\eta/\varkappa T$, where T is the temperature of the medium, and in virtually all the situations that really occur $\tau_2 \gg \tau_1$.

Let us represent $\mathbf{f}$ in the form

$$\mathbf{f}[\mathbf{r}_1+\delta\mathbf{r}(t),\ \mathbf{r}_2,\ d\delta\mathbf{r}/dt] \approx \mathbf{f}(\mathbf{r}_1,\ \mathbf{r}_2,\ d\delta\mathbf{r}/dt)$$
$$+(\delta\mathbf{r}\nabla)\mathbf{f}(\mathbf{r}_1,\ \mathbf{r}_2,\ d\delta\mathbf{r}/dt), \quad |\delta\mathbf{r}| \ll |\mathbf{r}_1-\mathbf{r}_2|. \tag{3}$$

Here $\delta\mathbf{r}(t)$ has the meaning of an averaged displacement, i.e., of the integral over time of the averaged (over time intervals of the order of τ_1) velocity.

In the case when $\delta\mathbf{r}(t)$ is due to Brownian displacements, we can write

$$\left\langle \delta\mathbf{r}_i(t)\frac{d}{dt}\delta\mathbf{r}_j(t)\right\rangle = \lim_{t\to\infty}\left[\frac{1}{2t}\int_0^t \frac{d}{dt'}\delta\mathbf{r}_i^2(t')\,dt'\right]\delta_{ij}$$
$$= \lim_{t\to\infty}(2Dt\delta_{ij}/2t) = \varkappa T\delta_{ij}/6\pi R_1\eta; \tag{4}$$

here the angle brackets denote averaging over time at times much greater than τ_1 and D is the coefficient of diffusion of the Brownian particle. Averaging (3) with allowance for

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(4), we obtain

$$\mathbf{F}=-\nabla U_{\text{eff}}, \quad U_{\text{eff}}=\frac{9}{16}\frac{R_1R_2}{|\mathbf{r}_1-\mathbf{r}_2|^2}\varkappa T, \tag{5}$$

where **F** is the averaged force and U_{eff} is the effective potential. Thus, there arises between the particles a repulsive potential that falls off with distance like r^{-2}, but the energy of this interaction is smaller than $\varkappa T$.

Let us also consider the problem of the interaction of a particle with a plane. The force **f** in this case can be represented in the form

$$\mathbf{f}(z, \mathbf{v}_0)\approx-6\pi R_1\eta\{(3/2\pi)\int ds(\mathbf{r}_1-\mathbf{r})(\mathbf{n}_0(\mathbf{r}_1-\mathbf{r})) \times((\mathbf{r}_1-\mathbf{r})\mathbf{v}'(\mathbf{r}))/|\mathbf{r}_1-\mathbf{r}|^5\}\approx-6\pi R_1\eta(9R_1\mathbf{v}_0/8z). \tag{6}$$

Here $\mathbf{n}_0$ is the unit vector perpendicular to the plane, **r** specifies the points on the plane, the integration is over the entire surface, and z is the distance from the particle to the wall. Averaging (6), we find

$$U_{\text{eff}}=9R_1\varkappa T/8z. \tag{7}$$

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