Langevin equation in the case of total accommodation

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The Langevin equation is derived for Brownian particles (BP) in a strongly rarefied classical gas (CG) for the cases of elastic and inelastic (total accommodation) of the interactions between the BP and the CG. Explicit expressions are obtained for the friction coefficient and for the random force, and the correlation function of the random forces is calculated. It is shown that the second fluctuation-dissipation theorem and the energy-distribution law are satisfied for elastic interactions, and also for rotation in the case of total accommodation, but are violated for translational motion under certain conditions. The causes and consequences of this effect are discussed.

Boris and Galkin[1] have recently derived a Fokker–Planck equation for Brownian particles (BP) in a strongly rarefied classical monatomic gas (CG) for the case of absolutely inelastic collisions between the BP and the CG, i.e., for total accommodation. The expressions obtained for the friction and diffusion coefficients of the translational motion do not satisfy the second fluctuation-dissipation theorem (FTD II), but this has not been noted by the authors.

Kravtsov *et al.*[2] have investigated two-dimensional diffusion of classical particles in the presence of a weak randomly nonpotential force with long-range correlation. They have found that FDT II is satisfied only if the temperature is renormalized.

We describe below a very simple derivation of the Langevin equation for the case of elastic and inelastic interaction between BP and a strongly rarefied CG, and calculate the friction coefficient and the correlation function of the random forces. In the case of inelastic interaction the FDT II is not satisfied for translational motion under certain conditions. The causes and consequences of this violation are discussed.

1. TOTAL AVERAGE FORCE

In Ref. 3 is derived an expression for the total time-averaged force (see below) exerted, in the case of total accommodation, on a surface element *dydz* of a moving body by a strongly rarefied CG with Maxwellian velocity distribution. Without repeating the calculations, we present only the results and discuss the conditions under which they are applicable when the body is a BP.

In the local coordinate frame of the surface element of a body moving with velocity **V**, the distribution function is

$$f=\text{const}\cdot\exp\left\{-\frac{\varepsilon_{\text{Ext}}}{kT}-\frac{m}{2kT}[(v_x-V_x)^2+(v_y-V_y)^2+v_z^2]\right\}, \tag{1}$$

where V_x and V_y are the BP normal and tangential velocities. In the case of total accommodation, the reflected CG particles have a Maxwellian distribution with $\mathbf{V}=0$. Only the incoming CG particles contribute therefore to the average tangential force per unit area.

$$\int mv_yv_xfd\Gamma=mV_y\int_0^\infty v_xf\,d\Gamma, \tag{2}$$

or

$$F_y=\theta V_y, \tag{3}$$

where

$$\theta=m\bar{j}_x=p(m/2\pi kT)^{1/2}, \tag{4}$$

$\bar{j}_x$ is the density of the average CG flux in the x (normal) direction, and p is the CG pressure.

The contribution of the incoming CG particles to the normal component of the average force is

$$\int mv_x^2fd\Gamma=\frac{p}{2}+p\left(\frac{2m}{\pi kT}\right)^{1/2}V_x, \tag{5}$$

and that of the reflected particles is

$$\frac{p}{2}+\frac{p}{2}\left(\frac{\pi m}{\pi kT}\right)^{1/2}V_x. \tag{6}$$

The last expression is obtained from a Maxwell distribution with $\mathbf{V}=0$ but so normalized that

$$\bar{j}_xV_x=-\bar{j}_x'V_x, \tag{7}$$

i.e., the average flux of the CG particles incoming on any surface element is equal (but opposite) to the average flux of the outgoing particles.

We consider hereafter, for simplicity, planar BP and assume that they are spontaneously magnetized in a direction perpendicular to their planes. If such BP are located in a sufficiently strong external magnetic field **B**, the only important forces are the normal ones for motion along **B**, and the tangential ones for motion perpendicular to **B**.

We get then from (4)–(6) for the friction forces

$$\mathbf{F}_\perp=\sigma_\perp\mathbf{V}_\perp, \tag{8}$$

$$F_\parallel=\sigma_\parallel V_\parallel, \tag{9}$$

where

$$\sigma_\perp=2S\theta, \tag{10}$$

$$\sigma_\parallel=2S\delta, \tag{11}$$

$2S$ is the total surface area of the planar BP, and

$$\delta={}^1/_2\theta(4+\pi), \tag{12}$$

$$\delta=4\theta=\delta_e \tag{13}$$

for total accommodation and elastic reflection, respectively.

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2. MODEL FOR TOTAL ACCOMMODATION

We assume that the total accommodation is due to the brief adsorption of the CG during an adsorption time τ_a in the BP adsorption potential (see, e.g., Ref. 4). To meet condition (7) we must therefore ensure satisfaction of the condition

$$[(\overline{\Delta r})^2]^{\tau_a} \ll r^2, \tag{14}$$

where r is the BP radius, i.e., the diffusion of the CG over the BP surface during the time τ_a can be neglected. It is necessary simultaneously to meet the condition

$$\tau_a \ll \tau_b, \tag{15}$$

where τ_b is the characteristic lifetime of the BP if the BP velocity is to remain constant during the time τ_a. If τ_0 is the average duration of one period of passage (or oscillation) in the adsorption potential and the following inequality is satisfied:

$$\tau_0 \ll \tau_a, \tag{16}$$

then the CG particle numbered i and having a velocity $\mathbf{v}_i$ will experience after the adsorption instant $t = t_i$ multiple reflections from the BP surface. Each reflection will cause redistribution of the energy and momentum among the individual atoms or groups of atoms on the BP surface before they are emitted at $t = '_i$ with velocity $\mathbf{v}_i'$, where

$$t_i' - t_i \sim \tau_a. \tag{17}$$

Obviously, the adsorption potential for the CG includes an intermediate random process during which the CG particle "forgets" its velocity for a time τ_0. In particular, the emitted particle has a new velocity $\mathbf{v}_i'$ prior to the adsorption. The incoming and outgoing CG particles are described then by Maxwellian distributions with equal temperatures. The total process—adsorption, intermediate random process, and emission—contains essentially random elements. Unlike elastic reflection, it cannot be described within the framework of only reversible classical (or quantum) mechanics. We therefore call this process "superstochastic."

3. RANDOM FORCE AND LANGEVIN EQUATION

To introduce the random force it must be remembered that the pressure [say in Eqs. (5) and (6)] is the result of many individual (elastic or inelastic) CG particle collisions, and is therefore a fluctuating quantity. If the conditions (14)–(16) are met, we can write for the normal component of the momentum imparted to an immobile BP by the CG during a time dt, in the case of inelastic interaction,

$$F(t)\,dt = m\Big\{\sum_i [\delta(t-t_i)v_i + \delta(t-t_i')v_i'] - \sum_k [\delta(t-t_k)v_k + \delta(t-t_k')v_k']\Big\}\,dt \tag{18}$$

$(v_i, v_i', v_k, v_k' > 0)$, whereas for elastic interaction

$$F(t)\,dt = m\Big\{\sum_i \delta(t-t_i)2v_i - \sum_k \delta(t-t_k)2v_k\Big\}\,dt. \tag{19}$$

For the tangential component we have

$$\mathbf{F}_\perp(t)\,dt = m\Big\{\sum_i [\delta(t-t_i)\mathbf{v}_{i\perp} + \delta(t-t_i')\mathbf{v}_{i\perp}'] - \sum_k [\delta(t-t_k)\mathbf{v}_{k\perp} + \delta(t-t_k')\mathbf{v}_{k\perp}']\Big\}\,dt, \tag{20}$$

where the contribution from both sides of a planar BP is explicitly taken into account.[1)]

The momentum transferred in an elastic interaction is well known to be $2m\mathbf{v}_i$, whereas in the inelastic case it consists of two statistically independent contributions, $m\mathbf{v}_i$ (adsorption) and $m\mathbf{v}_i'$ (emission) [see (18)–(20)], which lead after averaging to the terms $p/2$ in expressions (5) and (6). The Langevin equation states that

$$dU + U\sigma dt = M^{-1}F(t)\,dt \equiv A(t)\,dt \tag{21}$$

for the normal velocity of the BP ($U = V_x, \sigma = \sigma_\parallel/M, M$ is the BP mass). It is easy to show that

$$\overline{U(t)U(t+\tau)} \equiv \lim_{\vartheta\to\infty}\frac{1}{\vartheta}\int_{-\vartheta/2}^{\vartheta/2} dt\,U(t)U(t+\tau) = \int_{-\infty}^{+\infty}\frac{d\omega}{2\pi}|\alpha(\omega)|^2 e^{i\omega\tau}C(\omega), \tag{22}$$

where

$$C(\omega) = \int_{-\infty}^{+\infty} d\tau\, C(\tau)e^{-i\omega\tau} = C(-\omega), \tag{23}$$

$$C(\tau)\,d\tau = \overline{A(t)A(t+\tau)}\,d\tau = \lim \frac{1}{\vartheta}\int_{-\vartheta/2}^{\vartheta/2} dt\,A(t)A(t+\tau)\,dt, \tag{24}$$

$$\alpha(\omega) = 1/(-i\omega+\sigma). \tag{25}$$

It is known that the Langevin equation leads directly to the relation[5]

$$C(\omega) = 2\sigma(\omega)\overline{U^2(t)} = 2\sigma(\omega)\overline{U}^2, \tag{26}$$

which we call the FDT II of statistical mechanics. Following the usual application of the energy equipartition law $M\overline{U}^2 = kT$ or its equivalents, expression (26) becomes

$$C(\omega) = 2\sigma(\omega)kT/M, \tag{27}$$

which we shall call the FTD II of statistical thermodynamics.

4. CORRELATION FUNCTION OF A RANDOM FORCE

Using (18)–(20), we can now calculate the correlation function (24) for different cases.

4.1. Elastic Interaction

It follows in this case from the definition (24) that

$$C(\tau)\,d\tau = \lim_{\vartheta\to\infty}\frac{1}{\vartheta}\int_{-\vartheta/2}^{\vartheta/2} dt\,A(t)A(t+\tau)\,d\tau$$

$$= \lim_{\vartheta\to\infty}\frac{1}{\vartheta}\int_{-\vartheta/2}^{\vartheta/2} dt\Big(\frac{m}{M}\Big)^2\Big[\sum_i \delta(t-t_i)2v_i - \sum_k \delta(t-t_k)2v_k\Big] \times\Big[\sum_j \delta(t+\tau-t_j)2v_j - \sum_l \delta(t+\tau-t_l)2v_l\Big]\,d\tau, \tag{28}$$

and it must be recognized here that for a set of random times we have

$$\{t_i\}=\{t_j\}\neq\{t_k\}=\{t_l\}, \tag{29}$$

since the subscripts i and j number particles that collide from one side, and k and l from the other. A distinction must therefore be made between the diagonal ($i=j$, $k=l$) and nondiagonal contributions:

$$C(\tau)\,d\tau=4\left(\frac{m}{M}\right)^2 \times\lim\frac{1}{\vartheta}\int_{-\vartheta/2}^{\vartheta/2} dt\Big\{\Big(\sum_i\delta(t-t_i)v_i^2+\sum_k\delta(t-t_k)v_k^2\Big)\delta(\tau)$$
$$+\Big[\sum_{i\neq j}\delta(t-t_i)\delta(t+\tau-t_j)v_iv_j-\sum_{i,l}\delta(t-t_i)\delta(t+\tau-t_l)v_iv_l\Big]$$
$$+\Big[\sum_{k\neq l}\delta(t-t_k)\delta(t+\tau-t_l)v_kv_l-\sum_{k,j}\delta(t-t_k)\delta(t+\tau-t_j)v_kv_j\Big]\Big\}d\tau. \tag{30}$$

Since all the collisions in the CG are statistically independent, the contributions in the square brackets of (30) vanish individually upon integration. The result is

$$C(\tau)\,d\tau=4\left(\frac{m}{M}\right)^2\Big(\overline{\sum_i\delta(t-t_i)v_i^2}+\overline{\sum_k\delta(t-t_k)v_k^2}\Big)\delta(\tau)\,d\tau. \tag{31}$$

Recognizing also that

$$\overline{\sum_i\delta(t-t_i)v_i^2}=\overline{\sum_k\delta(t-t_k)v_k^2}=Sn\int_0^\infty f(v)v^3\,dv\equiv Sn\overline{v^3}/2, \tag{32}$$

we obtain ultimately for the correlation function of the random acceleration (force) in the case of a Maxwell distribution

$$C(\tau)\,d\tau=2(kT/M)\sigma_e\delta(\tau)\,d\tau\equiv C_e(\tau)\,d\tau, \tag{33}$$

where

$$\sigma_e=2S\delta_e \tag{34}$$

is the friction coefficient for the normal force in the elastic case. We emphasize that the temperature T enters in (33) only via the Maxwell distribution of $f(v)dv$ in (32) for a CG, with no additional assumptions whatever for the BP.

Comparison of Eq. (33) with (26) and (27) shows that the statistical-thermodynamics FDT II is satisfied for the normal velocity component if the CG particles are elastically reflected from the BP surface. We have obtained this result without invoking the classical-statistics equipartition law, which is confirmed on the one hand once more by our method and emphasizes on the other hand the correctness of our approach.

4.2. Inelastic Interaction (Total Accommodation)

Starting from expression (18) for the random force and using the same procedure, we obtain for the correlation function of the random acceleration (force) in inelastic interaction

$$C(\tau)\,d\tau=\lim_{\vartheta\to\infty}\frac{1}{\vartheta}\int_{-\vartheta/2}^{\vartheta/2} dt\left(\frac{m}{M}\right)^2\Big\{\sum_i[\delta(t-t_i)v_i+\delta(t-t_i')v_i']-\sum_k[\delta(t-t_k)v_k+\delta(t-t_k')v_k']\Big\}$$
$$\times\Big\{\sum_j[\delta(t+\tau-t_j)v_j+\delta(t+\tau-t_j')v_j']-\sum_l[\delta(t+\tau-t_l)v_l+\delta(t+\tau-t_l')v_l']\Big\}d\tau. \tag{35}$$

For the same reasons as in Sec. 4.1, we must distinguish between the diagonal ($i=j$, $k=l$) and nondiagonal contributions. The diagonal contributions yield

$$C(\tau)\,d\tau=\lim_{\vartheta\to\infty}\frac{1}{\vartheta}\int_{-\vartheta/2}^{\vartheta/2} dt\left(\frac{m}{M}\right)^2 \times\Big\{\Big[\sum_i\delta(t-t_i)v_i^2+\sum_i\delta(t-t_i')v_i'^2 \tag{36}$$
$$+\sum_k\delta(t-t_k)v_k^2+\sum_k\delta(t-t_k')v_k'^2\Big]\delta(\tau)$$
$$+\sum_i\delta(t-t_i)\delta(t+\tau-t_i')v_iv_i'$$
$$+\sum_i\delta(t-t_i')\delta(t+\tau-t_i)v_i'v_i+\sum_k\delta(t-t_k)\delta(t+\tau-t_k')v_kv_k'$$
$$+\sum_k\delta(t-t_k')\delta(t+\tau-t_k)v_k'v_k\Big\}d\tau.$$

It follows from (17) and (15) [see also (22)–(25)] that in the second group of terms in (36) we can make, for example, the substitution

$$\delta(t-t_i)\delta(t+\tau-t_i')=\delta(t-t_i)\delta(\tau+t_i-t_i')\approx\delta(t-t_i)\delta(\tau). \tag{37}$$

Recognizing in addition that for total accommodation we have, as indicated in Sec. 2,

$$\overline{\sum_i\delta(t-t_i)v_i^2}=\overline{\sum_i\delta(t-t_i')v_i'^2}$$
$$=\overline{\sum_k\delta(t-t_k)v_k^2}=\overline{\sum_k\delta(t-t_k')v_k'^2}\sim\overline{v^3}, \tag{38}$$

$$\overline{\sum_i\delta(t-t_i)v_iv_i'}=\overline{\sum_i\delta(t-t_i')v_i'v_i}=\overline{\sum_k\delta(t-t_k)v_kv_k'}$$
$$=\overline{\sum_k\delta(t-t_k')v_k'v_k}=\overline{\sum_k\delta(t-t_k')v_k'}\,\overline{v_k}\sim\overline{v^2}\,\overline{v}$$

and

$$\overline{v^2}\overline{v}=\overline{v^3}/2 \tag{39}$$

for a Maxwell distribution, we obtain ultimately

$$C(\tau)\,d\tau={}^3/_4C_e(\tau)\,d\tau, \qquad (40)$$

where C_e is defined in (33).

Integration of the nondiagonal contribution with respect to time

$$\lim_{\vartheta\to\infty}\frac{1}{\vartheta}\int_{-\vartheta/2}^{\vartheta/2}dt\Big\{\Big[\sum_{i\neq j}\Big(\delta(t-t_i)v_i+\delta(t-t_i')v_i'\Big)\Big(\delta(t+\tau-t_j)v_j+\delta(t+\tau-t_j')v_j'\Big)-\sum_{i,l}\Big(\delta(t-t_i)v_i+\delta(t-t_i')v_i'\Big)\Big(\delta(t+\tau-t_l)v_l+\delta(t+\tau-t_l')v_l'\Big)\Big]$$

$$+\Big[\sum_{k\neq l}\Big(\delta(t-t_k)v_k+\delta(t-t_k')v_k'\Big)\Big(\delta(t+\tau-t_l)v_l+\delta(t+\tau-t_l')v_l'\Big)-\sum_{k,j}\Big(\delta(t-k_k)v_k+\delta(t-t_k')v_k'\Big)\Big(\delta(t+\tau-t_j)v_j+\delta(t+\tau-t_j')v_j'\Big)\Big]\Big\}d\tau,$$

causes the two expressions in the square brackets to vanish separately, for the same reasons as in the elastic case [cf. (30)]. The fact that each factor consists of two contributions (from adsorption and emission) has no effect whatever on this result, sincle the complete statistical independence is preserved for $i\neq j$, $k\neq l$ and $i, l; k, j$.

With allowance for (12), (13), (26) and (33) it follows from (40) that

$$C(\tau)\,d\tau={}^3/_4C_e(\tau)\,d\tau={}^1/_4\overline{U^2}(4+\pi)\sigma_e\delta(\tau)\,d\tau, \qquad (41)$$

whence

$$\frac{\overline{U^2}}{kT/M}=\frac{6}{4+\pi}=0.840. \qquad (42)$$

We have found thus that for total accommodation neither the thermodynamics FDT II nor the energy equipartition law is satisfied for (the normal component of) translational motion of BP. We emphasize, however, that this conclusion is valid only if conditions (14)–(16) are met. If we have in place of (14)

$$[\overline{(\Delta r)^2}]^{\tau_a}\gg r^2, \qquad (43)$$

diffusion on the BP surface causes the average flux of emitted CG particles to be the same in all directions. In this case, obviously, the friction coefficient σ and the random-force correlation functions turn out to be, in like manner, equal to half the corresponding elastic values, and the FDT II is satisfied also for the normal velocity component. Note that for microscopic BP (e.g., heavy molecules) the condition (14) is not met at all, so that the FDT II for "micro-objects" is always satisfied also in the inelastic case.

It can thus be concluded that the macroscopic features of the BP [condition (14)] are the main cause (in conjunction with inelasticity) of the violation of the FDT II.

5. CONCLUSION

We have derived on the basis of our simple approach the Langevin equation for Brownian particles in a strongly rarefied classical gas. We were able to determine the friction coefficient and the random force for elastic and inelastic interactions between the BP and the CG. We have introduced for the inelastic case (total accommodation) a simple adsorption model that explains, on the microscopic level, the processes in total accommodation. Calculation of the correlation function for the random force and the friction coefficient has shown that the statistical-thermodynamics FDT II and energy equipartition law are satisfied in elastic interaction. In total accommodation, both laws are satisfied also for the tangential component of the velocities (rotation), and under condition (43) they are satisfied also for the normal velocity component, i.e., for translational BP motion, but are violated if conditions (14)–(16) are met. In the latter case the "macroscopicity" of the BP [see (14)] plays the decisive role.

It follows from the results that when (42) is met the kinetic (osmotic) pressure of flat ferromagnetic BP aligned in an external magnetic field [cf. the text following Eq. (7)] is smaller along **B** than in the perpendicular direction. Recognizing also that any infinitesimally slow rotation of the volume containing the BP (or rotation of the magnetic field) can be effected without loss of energy, it follows perforce that it is possible in principle to eliminate the difficulties connected with thermal effects.

The causes of such a possibility, in our opinion, are on the one hand the connection between the macroscopic properties [condition (14) and the ferromagnetism] of the BP jointly with the total accommodation, and on the other hand the fact that the microscopic energy kT is after all not a negligibly small quantity for BP.

We emphasize once more that our approach yields the conventional results for elastic interaction in any case. The same follows in the case of total accommodation for rotational and translational motion if condition (43) is met.

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1) Replacement of the δ functions by functions of finite width has no effect whatever on the derivations that follow.

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