Self-Motion in Physico-Chemical Systems Far from Thermal Equilibrium

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Abstract

Small physical objects can induce and maintain their own motion by releasing a chemical substance which changes the local properties of the medium. The collective behaviour of self-moving physical objects resembles the behaviour found in much more complex biological populations, such as the insect societies

1. Introduction

An important property of many biological organisms consists in their ability to actively move themselves through the medium (Berg,1978). This motion is induced by the processes which take place inside the living beings which represent open systems far from thermal equilibrium. It is found at different levels of the biological hierarchy, from bacteria to animals. Collective interactions in large ensembles of actively moving living objects can lead to emergence of complex coherent spatio-temporal structures, the typical examples of which are provided by the behaviour of the insect societies (Pasteels and Deneubourg, 1987; Gordon et al., 1992) and of the fish schools (Huth and Wissel, 1992)

The actual mechanisms of self-motion of even single living cells are very complicated (Berg, 1978; Carter, 1967; Parcell, 1977). Moreover, the motion of biological objects depends on a combination of a large number of factors and cannot be often experimentally controlled. To investigate the general properties of spatio-temporal pattern formation by the interacting ensembles of self-moving particles, it is better to perform firstly the analysis for the physico-chemical systems where the laws of motion of individual particles and of the interactions between them are well-known and can be quantitatively formulated.

Below we consider several simple physico-chemical systems which possess the property of self-motion. In our examples the motion of small particles, intended to model the individual biological organisms, involves surface forces which are known to sensitively depend on the chemical concentrations and on the temperature. Almost two decades ago (Greenspan, 1978) suggested that the slow creeping motion of liquid drops on the nonuniformly coated horizontal surfaces, which is induced by a gradient in the chemical concentration of the surfactant, can be used as a simple model for the biological effect of chemotaxis. Furthermore, it is known that, when a solid particle is placed in a liquid with a gradient of a chemical substance, it can begin to move along the direction of the gradient (Anderson et al., 1982; Dukhin and Derjaguin, 1974). The origin of this effect is similar to that of the Maragnoni instability: it occurs because the solvent changes the intensity of the surfaces forces applied at the liquid-solid interface, i.e. it influences the local surface tension coefficient of the liquid. Because of the gradient in the chemical concentration, the surface tension forces acting on the particle are not balanced and it moves along the direction of change of the chemical concentration. A closely related effect is observed in presence of a temperature gradient, since the surface tension coefficient has a strong temperature dependence. In the experiments (Young et al., 1959) small air bubbles in an oil slowly drifted to the hotter region. The velocity of the drift induced by a weak chemical gradient was estimated in (Anderson et al., 1982; Derjaguin and Dukhin, 1971). Chemical gradients can also induce motion of small drops on solid substrates. The drift of a small droplet placed on a flat horizontal solid surface covered by a surfactant whose concentration changes along a certain direction was theoretically investigated in (Greenspan, 1978). In the experiments described in (Bascom et al., 1964) "skating" of drops was observed which was induced by nonuniform evaporation changing the local concentration of the volatile surfactant in different parts of the drop and thus varying the local surface tension.

In the above examples, the physical motion of macroscopic particles is induced by externally imposed gradients. However, they provide us with an insight of how elementary *self*-moving objects can be constructed: to maintain their motion such objects should be endowed with an abilility to generate a local gradient of a chemical surface-active substance in the region around them.

There is a small experiment, often used as a lecture demonstartion, which impements this idea. Let us take a match stick that floats on the surface of water and attach a tiny piece of soap to its head. The stick immediately starts

to glide over the water surface and continues to move along a complicated trajectory until the soap is finally spent. A more interesting physical situation is found, if we take, instead of a stick, a small solid disc and attach soap under its bottom at the disc's center. Now, if the disc rests, it produces a symmetrical surfactant distribution and, therefore, the net capillary force vanishes. Suppose, however, that the disc moves along a certain direction. Then the surfactant concentration distribution around the disc becomes asymmetrical (the concentration is smaller at the front border and larger at the rear side). Hence, the local values of the capillary coefficient there are different and a net force, applied to the disc, arises. If the concentration dependence of the capillary coefficient is such that the resulting force acts in the direction of motion and the force is strong enough, it can balance the viscous friction and maintain further motion of our solid particle. Clearly, this motion could continue only while a particle releases the surfactant. However, if the surfactant is permanently produced inside this particle (or fed into it from an external source), the process can go on indefinitely long.

Alternatively, one can imagine a situation where it is not the particle which supplies the energy, but the liquid itself. Suppose, for instance, that this liquid contains a mixture of chemical reagents, such that a reaction between them can produce a surfactant. However, this reaction could take place only in presence of a solid surface catalyst. Assuming that such a catalyst is attached to the bottom point of a floating particle, we again come to the case that was described above.

Furthermore, it is not even essential that some surfactant is permanently produced. Instead, the temperature dependence of the capillary coefficient can be used. Namely, suppose that heat is continuously generated in the central bottom area of the considered particle. Then, if the particle moves, the temperature varies along its border (being larger in the rear side and smaller at the front). This again leads to a net capillary force which is able to keep the particle in motion.

Another possibility of self-motion involves slow crawling movement of liquid drops on solid surfaces. We consider a situation where a droplet contains a surfactant which, once a given area is covered by the droplet, is absorbed to the liquid-solid interface and changes the wetting properties of the surface. Because the properties of the surface are modified by the liquid cover, the magnitude of the capillary force at the contact line between the liquid and the (bare) solid surface depends on whether the liquid spreads to a new area or it retracts from the region which it has covered before. As was pointed out in (de Gennes, 1985), one can observe in this case that a drop first spreads over the solid surface and then it begins to retract. This happens under the conditions of partial wetting, if the equilibrium contact angle for a surface with the absorbed surfactant is larger than in its absence. However, this is not the only possible kind of the dynamical behavior. Suppose that at the beginning we have set the droplet into a translational motion (for instance, by slightly tilting the underlying surface and then returning it to the horizontal position). Then the front side of the droplet experiences the wetting conditions characteristic for the bare surface, whereas the rear side of it is retracting from the area previously covered by liquid and, hence, with the modified wetting properties. As a result, there is a net capillary force applied to the droplet as a whole and acting along the direction of motion. Because of this force, the droplet can continue its crawling motion.

A crawling droplet leaves behind it a trail of absorbed surfactant. The presence of this trail will be felt by other droplets, when they cross it in the process of their motion. To eliminate the resulting long-time memory, one can introduce a recovery mechanism. The absorbed surfactant is then gradually destroyed when it is no longer in contact with the liquid (e.g. due to a reaction with the gaseous atmosphere).

Remarkably, the self-motion of a droplet will resemble the propagation of a pulse in an excitable medium (observed, e.g., for the Belousov-Zhabotinskii

reaction). Here, the propagating pulse produces an inhibitor substance which triggers the reverse transition and afterwards gradually disappears, so that the initial state of the medium is recovered. However, the travelling pulse represents only an advancing concentration profile, whereas in the case of a droplet we have a real motion of a certain physical object. Moreover, instead of diffusion the principal role is played now by the capillary force which propels the droplet.

2. Gliding Bugs

The dynamical equations which govern self-motion of simple physico-chemical objects can be easily constructed. Consider, for instance, small solid particles ("bugs") which float on the surface of a liquid and gradually generate a substance that diffuses in the liquid and serves as a surfactant. For definiteness, we assume that each of the particles represents a small solid disc of radius R_0. The particles float on the surface of an infinite layer of liquid. Some chemical substance is permanently produced (at a rate J per unit time) in the particle and enters the liquid at the center point in the bottom of the disc. This substance diffuses in the liquid with a bulk diffusion constant D. Once dissolved, the substance modifies the local capillary coefficient Γ (which represents the force acting per unit length of the liquid- solid contact line). We assume that the concentration dependence of this coefficient is linear, i.e. $\Gamma = \Gamma_0 - \mu c$ where c is the surfactant concentration and μ is a positive constant.

When a bug is at rest, the concentration distribution around it is symmetrical and the capillary forces are balanced. However, when it moves, the concentration distribution becomes distorted which causes the appearance of a net force acting on this solid particle. The concentration distribution produced by a moving point-like source is described by equation:

$$c = D\Delta c + J\delta(\mathbf{r} - \mathbf{R}(t)) \quad . \tag{1}$$

If the source moves on the surface of the medium that occupies half-space, the solution reads as

$$c(\mathbf{r},t) = 2 \int_{\infty}^{t} dt' \, J \, G(\mathbf{r} - \mathbf{R}(t'), t - t') \tag{2}$$

where $G(\mathbf{r},\tau) = (4\pi D\tau)^{-3/2} \exp(- r^2/4D\tau)$ is the Green's function for diffusion.

Suppose that the source moves at a constant velocity V along the x-direction in the surface plane. Substituting $\mathbf{R}(t) = (Vt,0,0)$ into (2) and performing integrations, we find

$$c = (J/2\pi D\rho) \exp[-(V/2D)(x - Vt)] \exp(-\rho V/2D) \tag{3}$$

where $\rho = [(x - Vt)^2 + y^2 + z^2]^{1/2}$. This distribution is asymmetric: the surfactant concentration c is smaller in front of the moving source (for $x > Vt$) than at the same distance behind it.

The capillary forces act at the contact line between the solid and the liquid. The force dF, which acts on a contact line element dl, is equal to $dF = \Gamma dl$ and is directed along the normal to the contact line. The net capillary force can be calculated by summing the forces applied to all the elements of the solid-liquid border. If a bug represents a disc of radius R_0, the concentration distribution along its border is described by (3) where we should put $\rho = R_0$. Since we assume that the capillary coefficient Γ depends linearly on c, the net capillary force (directed along the x-axis) can be found by a simple integration which yields (in the limit of slowly moving bugs, $VR_0/2D << 1$)

$$F = (\mu J/2D)(VR_0/2D)[1 - VR_0/2D] \; . \tag{4}$$

Besides of the net capillary force, the bug experiences as well a viscous friction force F_v which is a certain function of its velocity V. For the large velocity, when the flow produced by a floating bug becomes turbulent, the dependence $F_v(V)$ is complicated. For smaller velocities, i.e. at low Reynolds numbers, this force should be (Landau and Lifshitz, 1959) proportional to V, i.e. $F_v = \zeta\eta V R_0$ where η is the fluid viscosity and ζ is a numerical proportionality factor. In the steady regime, the viscous friction compensates the net capillary force, so that $F = F_v$. Therefore, the velocity of steady motion is given by

$$V_0 = (2D/R_0)\,[1 - 4\zeta(\eta D^2/\mu J)]\,. \qquad (5)$$

We see that the bug can maintain its self-motion only if the rate J of the surfactant's production exceeds a certain threshold value $J_0 = 4\zeta(\eta D^2/\mu)$. Note that the velocity V_0 of steady self-motion is inversely proportional to the bug's radius R_0, whereas the threshold J_0 does not involve R_0. It means that, if we have a system of bugs of different sizes, all of them start to move at the same generation rate J_0 of surfactant, although the established velocities of their motion will be different.

In the above example self-motion resulted from the ability of bugs to continuously release a surfactant into the liquid. However, the same effect can be observed as well in absence of any surfactant production. Instead we can make use of the fact that the capillary forces are sensitive to local temperature of the liquid.

Suppose that a bug represents a small solid disc which has a tiny heating element attached at its bottom center. Due to the process of thermal conduction in the liquid, this creates a certain temperature distribution around the bug. For a resting bug this distribution is simmetrical and the capillary forces equilibrate. However, when the bug moves, this distorts the temperature field and makes it asymmetric. In turn, this influences the values of the capillary coefficient along the bug's border and gives rise to a net capillary force which is able to support the gliding motion.

Although the physical mechanism of self-motion, which involves heat generation, is different from that analized above, the respective mathematical investigation can be performed in a closely related way. This follows from a mathematical analogy between the processes of diffusion and heat conduction. Indeed, if we interpret c in equation (2) and furtheron as local temperature and J as the rate of heat production by the bug, all our analysis remains equally applicable.

3. Crawling Drops

In this section we consider another example of self-moving physical objects which represent liquid drops on a flat solid surface. Suppose that a drop contains a surfactant which, when a given area of the surface is covered by the liquid, attaches to the solid surface and modifies its properties. We assume that the capillary coefficient Γ (which gives the force acting per unit length of the liquid-solid contact line) depends linearly on the surface concentration c of the absorbed surfactant and, furthermore, that it decreases with c as $\Gamma = \Gamma_0 - \mu c$.

When the drop moves, it experiences a larger value Γ_0 of the capillary coefficient at its front, where it enters the areas not previously covered by the liquid, and the smaller values of Γ at its back, where the absorbed surfactant is present. This results in a net capillary force which could keep the drop in motion.

We must specify the dynamics of the surfactant absorption. It is assumed that its amount in the drop is sufficiently large and that the exhaustion of the surfactant due to the absorption process can be neglected (or, alternatively, the surfactant is continuously supplied to the droplet). Furthermore, absorption is

supposed to be accompanied by the reverse desorption process so that, in the simplest approximation, the surface concentration c obeys the equation

$$\dot{c} = -\gamma(c - c_0) . \tag{6}$$

We do not take into account surface diffusion of the absorbed molecules.

It is assumed that the conditions of *partial wetting* are satisfied for the given liquid- solid interface, i.e. the resting drop represents a spherical cap which forms a small equilibrium contact angle θ_e with the solid surface (since $\theta_e << 1$, the cap looks more like a pancake). Note that, when the velocity is small enough, the influence of motion on the shape of the drop can be neglected. Below we assume that the drop has radius R_0 and maximal height $h_0 = \theta_e R_0/2$.

When the crawling motion is slow (namely, if $V << \gamma R_0$), the surfactant concentration at the rear side of the drop is equal to c_0, whereas at its front $c = 0$. Since the capillary coefficient Γ depends on c as $\Gamma = \Gamma_0 - c\mu$, the net capillary force applied to the drop is $F = 2\mu c_0 R_0$ and is independent of V.

It is a little more difficult to calculate the total force of the viscous friction which is experienced by the crawling drop. We can do this by first calculating the rate W of the energy dissipation in the moving drop and then using the relationship $W = F_v V$ to find the friction force F_v.

Since the crawling motion of the drop is slow, the hydrodynamical flows within the drop are characterized by low Reynolds numbers and we can neglect the inertial terms in the Navier-Stokes equation. Moreover, since the drop is a very thin "pancake", we can use the lubrication approximation (Landau and Lifshitz, 1959) so that the equation for the horizontal component v of the velocity field is simply

$$\partial^2 v/\partial z^2 = (1/\eta)\, \partial p/\partial x \tag{7}$$

where p is the local pressure and η is the viscisity coefficient. The boundary conditions can be easily formulated. We have $v(z=0) = 0$ because the horizontal velocity should vanish at the solid surface. The top layer of the liquid is free and hence we have $\partial v/\partial z = 0$ at $z = h$. The solution of (7) with these boundary conditions is

$$v(z) = -(1/2\eta) z(2h - z)\, \partial p/\partial x . \tag{8}$$

Hence, the average horizontal velocity is

$$\langle v \rangle = (1/h) \int_0^h v(z)\, dz = -(1/3\eta)\, h^2\, \partial p/\partial x . \tag{9}$$

If the drop moves as a whole at a constant velocity V, the average horizontal velocity $\langle v \rangle$ at each crosssection x should coincide with V, i.e. $\langle v \rangle = V$. This yields $\partial p/\partial x = -3V\eta/h^2$. Substituting this expression for the pressure gradient into (8), we obtain the velocity profile in the crawling drop

$$v(z) = (3/2) V z(2h - z)/h^2 \tag{10}$$

where h is the local thickness of the drop.

The rate W of the energy dissipation can be calculated, according to (Landau and Lifshitz, 1959), as

$$W = (\eta/2) \int (\partial v/\partial z)^2\, dx\, dy\, dz . \tag{11}$$

When the velocity profile is given by (10), this yields after an integration

over z

$$W = (3/2)V^2\eta \int h^{-1}\ dx\, dy\ . \qquad (12)$$

Since the drop thickness h vanishes at the contact line, the integral (12) logarithmically diverges on the border of the drop. The divergences of this kind have been extensively discussed in the literature (de Gennes, 1985; Huh et al., 1971; Dussan et al., 1991; de Gennes et al., 1990). They are related to the fact that the standard hydrodynamical description breaks down for very thin, almost monomolecular layers. Actually, the bottom layer of the liquid slips a little in respect to the underlying solid surface (Dussan et al., 1991). Moreover, in a close vicinity of the contact line one should take into account (de Gennes, 1985) the molecular van der Waals forces (which give rise to the so- called disjoining pressure). These effects can be phenomenologically incorporated into the hydrodynamical description by introducing an integration cutoff at a certain distance Δ from the contact line (this characteristic molecular length may be found from the micro- or mesoscopic theory, see [Dussan et al., 1991; de Gennes et al., 1990]).

When the velocity of crawling is small, we can neglect the distortions in the shape of the droplet and assume that $h = h_0(1 - \rho^2/R_0^2)$ where ρ is the distance from its center and $h_0 << R_0$. Substituting this into (12) we obtain, after an integration over the angle,

$$W = (3\pi\eta V^2/h_0) \int_0^{R_0 - \Delta} (1 - \rho^2/R_0^2)^{-1}\, \rho d\rho \approx (3\pi\eta V^2 R_0^2/2h_0) \ln(R_0/2\Delta)\ . \qquad (13)$$

Since $W = F_v V$, this gives us an expression for the viscous friction force

$$F_v = (3\pi\eta V R_0/\theta_e) \ln(R_0/2\Delta)\ . \qquad (14)$$

Here we have used the relationship $h_0 = \theta_e R_0/2$. Note that, similar to the case of floating bug, the viscous friction force is proportional to the velocity V of motion, the viscosity coefficient η and the radius R_0 of the droplet.

In the steady regime of crawling, the capillary force is balanced by the viscous friction force, i.e. $F = F_v$. This yields the velocity of steady crawling

$$V = (2\mu c_0\theta_0/3\pi\eta)\ [\ln(R_0/2\Delta)]^{-1}\ . \qquad (15)$$

Remarkably, the velocity of slow crawling depends only weakly (i.e. logarithmically) on the radius R_0 of the drop.

In our analysis of crawling drops we have neglected spending of the surfactant in the process of adsorption. Although this might be a slow process, in reality the stored surfactant is gradually spent, so that its equilibrium surface concentration c_0 would become smaller and smaller. This will slow down the self-motion and eventually terminate it. Hence, the phenomenon of self-motion for the considered liquid drops represents a transient process. Howeever, it can be made indefinitely long if we could continuously supply the surfactant to the drop, in order to compensate for its spending.

As an alternative, one can consider another possible experimental set-up. Suppose that the properties of the *bare* surface are modified by the reactions with the gaseous atmosphere or, for instance, by the applied illumination. Now, when the droplet arrives and the surface becomes protected by the liquid layer, its properties undergo a transformation which may result in a decrease in the capillary coefficient. Then again the front and the back of the moving drop would experience different values of the capillary coefficient, i.e. Γ_0 at the front

and Γ' at the back. The above analysis is easily generalized to this case if we replace μc_0 by $\delta\Gamma = \Gamma_0 - \Gamma'$ in all relevant expressions.

Since this does not influence the motion of an individual drop, we did not explicitly consider in our analysis the processes which occur *after* the drop has passed through a given surface area. However, they may be important for interactions between the crawling drops. When the drop crawls, it leaves after it a trace where the properties of the surface are modified (e.g. due to the adsorbed surfactant molecules). The trace will be felt by other drops if their trajectories of motion intersect it. The trace is slowly destructed by the processes like desorption and the initial properties of the bare surface are recovered after some time.

4. Self-Motion in Presence of External Fields

A variety of external fields may act on self-moving objects. For instance, by supplying the surfactant from an external source, we can create its gradients on the surface and thus produce additional capillary forces that act on the bugs. General equations of self-motion in presence of an external force field **f** have the form

$$m\dot{V} = g(V)V/V + f \quad , \tag{16}$$

where m is the mass of a self-moving object. Function g(V) is given by difference of the self-moving (capillary) force F and the force of viscous friction F_v. It changes its sign at $V = V_0$ and becomes negative for $V > V_0$.

Suppose that a self-moving particle enters a region with a uniform external field **f** which is orthogonal to its initial direction of motion, so that $V(t=0) = (0,V_0)$ whereas $f = (f,0)$. Since the forces of self- motion determine only the magnitude, but not the direction of motion, even a weak external force **f** is sufficient to change the direction of the particle's motion and to orient it along the force **f**. Simple calculations show that time interval ΔT within which the self-moving particle completes the turn can be estimated as

$$\Delta T = mV_0/f \, . \tag{17}$$

This estimate holds for weak enough forces, such that the condition $|f| << g'(V_0)V_0$ is satisfied.

Suppose now that the external field is not uniform, i.e. $f = f(r)$. Let L be a characteristic length-scale for the spatial variation of f. A self-moving particle would take about $T = L/V_0$ to traverse the distance L. If the spatial variation of the external field is slow, the particle adjusts its direction of motion to the local direction of f(r). This happens if the characteristic turning time ΔT is much smaller than the time $T = L/V_0$ within which the force, experienced by the particle, remains approximately constant. Explicitly, this implies

$$|f| L >> mV_0^2 \, . \tag{18}$$

When the above condition is satisfied and the external force is given by a gradient of a certain potential U, so that $f = -\,\mathrm{grad}U$, the momentary velocity of the particle is simply

$$V = -V_0 \,\mathrm{grad}U/|\mathrm{grad}U| \, . \tag{19}$$

This means that the particle always moves along the direction of the gradient, but at a constant velocity V_0 that does not depend on its slope.

We consider next the case when f(t) is a delta-correlated random force, such that $\langle f \rangle = 0$ and

$$<f_\alpha(t)f_\beta(t')> = 2\sigma\, \delta_{\alpha\beta}\, \delta(t - t') . \tag{20}$$

The Fokker-Planck equation for the probability distribution $p = p(\mathbf{V},t)$ reads then as

$$\partial p/\partial t = - \partial[(g/Vm)\mathbf{V}p]/\partial \mathbf{V} + (\sigma/m^2)\partial^2 p/\partial \mathbf{V}^2 . \tag{21}$$

Introducing the polar coordinates by $V_x = V \cos\phi$ and $V_y = V \sin\phi$, we can write it in the form

$$\frac{\partial p}{\partial t} = - \frac{\partial}{\partial V}\left(\frac{g(v)}{m} p\right) + \frac{\sigma}{m^2 V} \frac{\partial}{\partial V}\left(V \frac{\partial p}{\partial V}\right) + \frac{\sigma}{m^2 V^2} \frac{\partial^2 p}{\partial \phi^2} . \tag{22}$$

Remarkably, this equation coincides with the Fokker-Planck equation which describes fluctuations near the generation threshold of a one-mode laser (Haken, 1975). In the latter case V is interpreted as an amplitude and ϕ as a phase of a generated light mode. When the threshold is passed, amplitude V experiences only small statistical variations around its steady value, whereas phase ϕ undergoes slow diffusion. Since this diffusion is slow, the phase remains almost constant within long intervals of time and, hence, the produced radiation is almost coherent. In the case of self-moving particles, the magnitude of the particle velocity above the threshold remains constant ($V \cong V_0$) whereas the direction of motion is not fixed. Application of a weak external force results then in diffusion-like process for the angle variable ϕ and in small variations of V around the steady value V_0.

When fluctuations of V are small, we can approximately replace V by V_0 in the last term in (22) and, after integration over V, derive a closed equation for the probability distribution $p(\phi,t)$ of the angle variable:

$$\partial p/\partial t = (\sigma/m^2 V_0^2)\, \partial^2 p/\partial \phi^2 . \tag{23}$$

Hence, the polar angle ϕ undergoes diffusion-like random wandering with an effective "angle-diffusion" constant $D_\phi = \sigma/m^2 V_0^2$. Note that far above the threshold, where the velocity V_0 of self-motion is large, the "angle-diffusion" constant D_ϕ becomes very small. It follows from (23) that $\phi(t)$ is a random Wiener process and that

$$<\phi^2(t)> = (\sigma/m^2 V_0^2)t . \tag{24}$$

Since the direction of motion changes randomly in time, the trajectory of motion is chaotic. The position of the particle at a time moment t is given by

$$\mathbf{r}(t) = \int_0^t \mathbf{v}(t')\, dt' = V_0 \int_0^t \mathbf{n}(t')\, dt', \tag{25}$$

where $\mathbf{n} = \mathbf{V}/V$ is a (random) unit vector specifying the direction of motion.

The mean-square displacement of the particle can be calculated as

$$<\mathbf{r}^2(t)> = V_0^2 \int_0^t \int_0^t dt_1\, dt_2\, <\mathbf{n}(t_1)\mathbf{n}(t_2)>$$

$$= V_0^2 \int_0^t \int_0^t dt_1\, dt_2\, <\cos \phi(t_1 - t_2)> . \tag{26}$$

Here $\phi(t_1 - t_2)$ is the angle between the directions of motion at time moments

t_1 and t_2. It is a random function of the difference $t_1 - t_2$. Since t_2 can be chosen as the initial time moment, the mean square of ϕ is given by (24) with $t = t_1 - t_2$.

Using the properties of the Wiener random processes, we find after a simple calculation that

$$<r^2(t)> = 2(V_0^4m^2/\sigma)t + (V_0^6m^4/\sigma^2)\{\exp[-(2\sigma/V_0^2m^2)t] - 1\} . \qquad (27)$$

We see that in the limit of large times ($t >> V_0^2/\sigma$) the diffusional law $<r^2(t)> = D_{eff}t$ holds, with an effective diffusion constant D_{eff} given by

$$D_{eff} = 2m^2V_0^2/\sigma . \qquad (28)$$

Hence, a self-moving particle performs random Brownian motion. It is instructive to compare D_{eff} with a diffusion constant D_0 for a Brownian motion of the *same* particles in absence of the self-propelling force. This process is described by the equation

$$m\dot{V} = -\gamma V + f(t) , \qquad (29)$$

where $F_v = -\gamma V$ is the force of viscous friction and the random force $f(t)$ is the same as in the equation (9). According to (29), the particle performs then the Brownian motion with a diffusion constant $D_0 = \sigma/\gamma^2$.

The diffusion constant is related to temperature θ by the Einstein law $D_0 = \theta/\gamma$. Comparing these two expressions, we find $\sigma = \theta^2/D_0$. Substituting this into (28) yields

$$D_{eff}/D_0 = 2(mV_0^2/\theta)^2 . \qquad (30)$$

To discuss the obtained results, we note that temperature specifies the mean kinetic energy of a Brownian particle, i.e. $\theta = m<V_x^2> = m<V_y^2> = (1/2)m<V^2>_\theta$, where $<V^2>_\theta$ is the mean-square thermal velocity of the particle. Therefore, the relationship (30) can be written as well in the form

$$D_{eff}/D_0 = (V_0^2/<V^2>_\theta)^2 . \qquad (31)$$

Hence, diffusion of a self-moving particle is enhanced by a factor which is a fourth power of the ratio between the steady velocity of established self-motion and the mean- square-root thermal velocity of the same particle in absence of self-motion. This factor can be very large. As a result, a self-moving heavy particle could perform a macroscopic diffusive motion even when its passive thermal diffusion is negligible.

5. Discussion

Above we considered several problems involving individual self- moving particles. In conclusion we want to discuss, in qualitative terms, what might be the statistical properties of large ensembles of such objects. The floating bugs are surrounded by clouds of the surfactant. Therefore, when one particle approaches another, it experiences an additional capillary force induced by the gradient of the surfactant that is produced by the second particle. This force is directed opposite to the direction of the gradient and leads, therefore, to repulsion between the bugs. The radius of action of the resulting repulsive forces can be roughly estimated as the size of a surfactant cloud.

Collisions between the bugs give rise to their scattering. This process resembles the standard scattering of two mechanichal particles with the only exception. Namely, instead of conservation of the sum of kinetic energies of

both involved particles, the kinetic energy of *each* of the particles remains the same as before the collision. Indeed, the magnitude (but not the direction) of velocity of a self-moving particle is quickly brought back to its steady value V_0 after any perturbation.

When the average distance between the bugs is much larger than the characteristic radius of action of the repulsive forces, the ensemble of such particles would behave like a weakly non-ideal two-dimensional gas where all the "molecules" have the same absolute value of velocity. The behavior of this system can be analyzed in the same way as that of the usual weakly non-ideal gases, by constructing a kinetic equation with an appropriate collision integral.

Consider now what could happen if we increase the density of such a gas, i.e. if we decrease the average distance between the bugs. When it becomes comparable with the characteristic radius of the surfactant "cloud", the ensemble would probably exhibit the properties which are more common for *liquid crystals*. Namely, there would be a tendency to form blocks of many individual particles which move almost in the same direction. One can also envisage a possibility of a phase transition which would result in the ordered motion of particles along a certain, arbitrarily taken, direction. It might be interesting to analyze further these opportunuties, e.g. by a computer simulation.

For the crawling drops the interactions are different. The properties of the underlying surface are changed only in the trails, left by a moving drop, but not in front of it. Hence, only when a drop crosses the trail left by another drop that has passed some time ago, it experiences an additional scattering force. The front collisions would result in merging of the two drops. Hence, the statistical mechanics of such an ensemble would be closer to that of the reacting gases.

We have shown in this paper how the accumulated, or permanently supplied, chemical energy can induce the mechanical motion of macroscopic objects. We assumed that the medium itself was inert, so that the objects pushed themselves through it. However, similar mechanisms may be employed to produce the mechanical motion of *inert* particles on top of a chemically active liquid medium. Suppose that some chemical reactions in a liquid result in appearence of travelling waves of chemical concentrations (as it is the case, for example, in the Belousov-Zhabotinskii reaction). If, furthermore, local changes of chemical concentrations modify the values of the capillary coefficient for a contact line between the liquid and the solid, their gradients could induce physical motion of small solid particles which float on top of the liquid layer. In this manner, travelling waves of chemical concentrations can be directly coupled to the mechanical motion.

There is yet another aspect which deserves a detailed investigation. In our analysis we assumed that the increased concentration of a surfactant diminishes the strength of the capillary forces and, hence, the capillary force applied to the front of an object is larger than that acting on its back. This resulted in motion of the considered objects. However, depending on the nature of a particular surfactant, a different situation is also possible. Namely, the surfactant can *increase* the capillary coefficient. Then the net capillary force is opposite to the direction of motion and, effectively, gives rise to an additional "friction" which makes much more difficult the motion of such an object over the underlying substrate. Using this phenomenon, one can almost rigidly attach solid bugs to the surface of a moving liquid or produce liquid droplets which remain almost immobile on the solid surface when it is tilted or shaked.

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