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Anomalous Slow Dewetting of Colloidal Particles at a Liquid/Gas Interface

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Abstract: We consider the anomalously slow dewetting of colloidal particles adsorbed at a liquid/gas interface. The particles move in the vertical direction under the action of a regular capillary force and an irregular force caused by defects (roughness and chemical heterogeneity). The particle diffusion is modeled by a random walk over a potential minima with jump rates determined by the Arrhenius law. The averaged particle motion is found under the assumption of Gaussian distributions for characteristic properties of spatial heterogeneities.

Keywords: colloidal particle; interfacial adsorption; anomalous diffusion

1. Introduction

The dynamics of contact line motion over a heterogeneous surface under the joint action of a deterministic force and the thermal noise is a challenging problem. The ingredients of the theoretical description of that motion are the hydrodynamic theory on all the scales from the capillary length scale to nanoscale [1] and the consideration of thermally activated jumps over molecular scale and nanoscale inhomogeneities [2]. The mathematical modeling has to be a combination of traditional hydrodynamic approaches (Stokes equation, lubrication approximation) and kinetic approaches (Langevin equation, Fokker-Planck equation, Kramers' theory, molecular dynamics) [3–6].

An important example of the contact line propagation on a solid substrate is the motion of a colloidal particle at the liquid interface, when the particle breaches the interface and tends to its equilibrium position. The theory predicts that in the absence of surface heterogeneities, a particle would reach its equilibrium position within a short viscous relaxation time. In reality, a solid surface is typically subject to roughness and chemical heterogeneities, which can lead to pinning of the contact line [7]. The dynamics of a colloidal particle near the interface was studied experimentally in [8–12]. The observed relaxation of the particle position is extremely slow, $x(t) \sim \ln(t/t_0)$ [10], where t_0 is a certain constant insignificant in the limit $t \gg t_0$. The motion of the contact line is due to thermal fluctuations that give rise to the escape of the particle from the potential wells over spatially irregular set of energy barriers [13]. Unlike the problem of the contact line propagation on a plane, where the most significant effect is the distortion of the contact line, the dominant effect is the *one-dimensional* motion of the particle towards the interface. Thus, one can expect that the latter problem is more tractable.

The phenomenon of anomalously slow, thermally induced motion of a Brownian particle in a spatially disordered environment is a subject of a vast literature (see, e.g., the review in Reference [14]). A prominent example of anomalously slow particle diffusion is Sinai's diffusion [15] of a particle under the action of a *force* which is a Gaussian white noise in space and time. The mean square displacement changes with

time as $\langle \delta x^2(t) \rangle \sim \ln^4(t/t_0)$, while a packet of particles moves according the law $\bar{x}(t) \sim \ln^2(t/t_0)$ [16]. These results ostensibly contradict the general theory, which predicts a normal diffusion law, $\langle \delta x^2(t) \rangle \sim Dt$, with the diffusion coefficient D reduced by the random environment [17]. In the case of Sinai's diffusion, the anomalous decrease of the diffusion rate is related to the unbounded spatial growth in the amplitude fluctuations of the potential $U(x)$. Indeed, for a spatial white noise of the force $F(x) = -dU(x)/dx$, $\langle U(x+x')U(x') \rangle \sim x^{1/2}$. Actually, even in the case where the potential $U(x)$ is a stationary Gaussian process with finite mean-squared fluctuations, the maximum amplitude of the potential's fluctuations grows at intermediate scales as:

$$|\delta U_{max}| \sim [\ln(x/x_0)]^\delta;$$

that leads to a *transient* anomalous diffusion:

$$\langle \delta x^2(t) \rangle \sim [\ln(t/t_0)]^{2/\delta},$$

where δ is a certain function of the distance (for details, see References [18,19]). A transient anomalous diffusion was observed in colloidal systems that evolve in random light fields [20,21].

The theoretical description of the thermally-activated colloidal particle motion based on the Kramers' theory has been done in [10,22]. In the case of a colloidal particle trapped in potential minima near the liquid/gas interface, an additional factor is the harmonic potential $U(x) \sim (x - x_0)^2$ created by the interfacial energy missing due to the particle adsorption. In Reference [22], a logarithmic law for the particle's position relaxation was found for a regular potential:

$$U(x) = \frac{1}{2}K(x - x_0)^2 + \frac{1}{2}\Delta U \sin(\lambda x + \phi),$$

where K , x_0 , ΔU , λ and ϕ are constants, by both analytical computation and direct simulation of the corresponding Langevin equation (see also References [11,12]).

In the present paper we consider the random walk of a colloidal particle between irregularly placed potential minima in the presence of an additional harmonic potential. The logarithmic relaxation law is confirmed.

2. Formulation of the Problem

First, let us consider a spherical particle of the radius R straddling the liquid/gas interface. The vertical coordinate of the particle center with respect to the liquid level is z , $|z| < R$. The area of the solid/liquid interface is $A_{sl} = 2\pi R(R + z)$, the area of the solid/gas interface is $A_{sg} = 2\pi R(R - z)$, and the area of the liquid/gas interface missing due to the particle adsorption is $A_- = \pi(R^2 - z^2)$. Therefore, the interfacial energy of the adsorbed particle is [23]:

$$U_0(z) = \gamma_{sl}A_{sl} + \gamma_{sg}A_{sg} - \gamma_{lg}A_- = \frac{1}{2}K(z - z_0)^2 + E_m, \quad (1)$$

where:

$$K = 2\pi\gamma_{lg}, \quad z_0 = \frac{\gamma_{sl} - \gamma_{sg}}{\gamma_{lg}}R = -R \cos \theta, \quad \text{and}$$

$$E_m = \pi\gamma_{lg} \left[- \left(\frac{\gamma_{sl} - \gamma_{sg}}{\gamma_{lg}} \right)^2 + \frac{2(\gamma_{sl} + \gamma_{sg})}{\gamma_{lg}} - 1 \right] R^2.$$

Here γ_{sl} , γ_{sg} , and γ_{lg} are solid/liquid, solid/gas, and liquid/gas interfacial tensions, respectively, and θ is the contact angle. One can see that the equilibrium energy of the particle adsorbed at the interface, E_m , is lower than the energy of particle in the liquid, $E_l = 4\pi\gamma_{sl}R^2$, and that in the gas, $E_g = 4\pi\gamma_{sg}R^2$:

$$E_m - E_l = -\frac{\pi R^2}{\gamma_{lg}}(\gamma_{lg} + \gamma_{sl} - \gamma_{sg})^2, \text{ and } E_m - E_g = -\frac{\pi R^2}{\gamma_{lg}}(\gamma_{lg} + \gamma_{sg} - \gamma_{sl})^2.$$

Therefore, the particle adsorption is always energetically favorable.

In reality, however, a particle is never perfectly spherical (because of its roughness), and the interfacial tensions γ_{sl} and γ_{sg} are not perfectly constant everywhere (due to chemical heterogeneity). Therefore, the energy of the particle, Equation (1), is perturbed. Later on, following Reference [22], we disregard the possible change of the energy by particle rotation and characterize the state of the particle by a single variable, $x = z - z_0$. Thus the energy of the particle is:

$$U(x) = E_m + \frac{1}{2}Kx^2 + V(x), \quad (2)$$

where $V(x)$ is a certain non-monotonic function determined by the irregularities of the particle surface. The *deterministic* force acting on the particle is:

$$F(x) = -\frac{dU}{dx} = -Kx + f(x), \quad (3)$$

where $f(x) = -dV(x)/dx$ is a sign-alternating function. In the region:

$$|x| < |f|_{max}/K, \quad (4)$$

where $|f|_{max}$ is the maximum value of $|f(x)|$, the function $F(x)$ has a sequence of zeros corresponding to minima and maxima of the potential (Equation (2)).

Assume that the particle is initially located in the liquid, hence its location $x(t) \leq 0$ for any time. Let us enumerate the zeros of $F(x)$ in the subregion with $x(t) \leq 0$ of the region in Equation (4) as:

$$x_N < \dots < x_1 < x_0. \quad (5)$$

Without loss of generality, assume that the points x_n with even n correspond to the minima of the potential, and those with odd n correspond to the maxima of the potential. Later on, we assume that N is large, and the distances between extrema of the potential are small.

If there are no thermal fluctuations, the dynamics of the particle are determined by:

$$\frac{1}{b} \frac{dx}{dt} = F(x),$$

where b is the mobility determined by the liquid viscosity (inertial effects can be neglected for colloidal particles). Therefore, for any initial position $x(0)$, the particle approaches the nearest minimum of the potential (at large t , the distance between the particle and the potential minimum point decreases exponentially with time) and stays there forever (pinning of the particle). The situation is different at a finite temperature T . The motion of the particle is governed by the Langevin equation:

$$\frac{1}{b} \frac{dx}{dt} = F(x) + \sqrt{\frac{2kT}{b}} \xi(t), \quad (6)$$

where k is the Boltzmann constant and $\zeta(t)$ is the unbiased white Gaussian noise, i.e.,

$$\langle \zeta(t) \rangle = 0, \quad \langle \zeta(t) \zeta(t') \rangle = \delta(t - t'). \quad (7)$$

Assume that for all equilibrium points in the sequence (5), the condition

$$|\Delta U(x_n)| \gg kT \quad (8)$$

is satisfied, where

$$\Delta U(x_n) \equiv U(x_n) - U(x_{n-1}).$$

We eliminate the pairs of points from the list in Equation (5) that do not satisfy the condition in Equation (8). In that case, the particle wanders between the minima of the potential, spending more time in the deeper wells. The motion of the particle can be presented as a random walk between the neighboring minima (points x_n with even n) with the jump rates $p(n \rightarrow n - 2)$ upward and $p(n \rightarrow n + 2)$ downward, which depend on the heights of the potential barriers according to the Arrhenius law [24]:

$$p(n \rightarrow n - 2) = C_n^- e^{\Delta U(x_n)/kT}, \quad p(n \rightarrow n + 2) = C_n^+ e^{-\Delta U(x_{n+1})/kT},$$

where the constants C_n^\pm depend on the details of the potential profile near the extremum points. Thus, the mean local (microscopic) velocity of the particle can be estimated as:

$$v_n = (x_{n-2} - x_n) C_n^- e^{\Delta U(x_n)/kT} - (x_n - x_{n+2}) C_n^+ e^{-\Delta U(x_{n+1})/kT}. \quad (9)$$

Note that both $\Delta U(x_n)$ and $-\Delta U(x_{n+1})$ are negative. The local velocity can significantly fluctuate from site to site, depending on the details of the potential shape for a definite colloidal particle. Our goal is to estimate the average velocity for an ensemble of particles with random locations of defects. We consider the motion of the particles far from the final equilibrium point, assuming $n \gg 1$.

3. Averaged Particle Dynamics

In order to find the average velocity, we take a number of assumptions. Their verification for real colloidal particles has to be based on measurements, which is beyond the scope of the present paper. It is assumed that the distances between particles are sufficiently large, therefore it is sufficient to consider the motion of a single particle moving independently of other particles. The distances between the adjacent potential extrema, $\Delta x_n = x_{n-1} - x_n$, are assumed to be independent, identically distributed, Gaussian random variables with a certain mean value $\Delta x = \langle \Delta x_n \rangle$ and dispersion $\sigma^2 = \langle (\Delta x_n - \langle \Delta x_n \rangle)^2 \rangle$, which are independent of n . Strictly speaking, the Gaussian distribution has to be cut off in order to avoid negative values of Δx_n . It is expected, however, that if σ is sufficiently smaller than Δx , the influence of that cutoff can be neglected. A similar assumption is taken for the corresponding value differences of the irregular part of the potential in adjacent minimum and maximum points; we assume that:

$$W(x_n) = |V(x_n) - V(x_{n-1})| = \bar{W} + \Delta W_n,$$

where ΔW_n are independent Gaussian random variables with $\langle \Delta W_n \rangle = 0$ and $\langle (\Delta W_n)^2 \rangle = \Sigma^2$. The variables Δx_n and ΔW_n are assumed to be mutually independent.

For this case:

$$x_n = x_0 - \sum_{i=1}^n \Delta x_i = x_0 - n\Delta x + \zeta_n,$$

where:

$$\zeta_n = -\sum_{i=1}^n (\Delta x_i - \Delta x) \sim \sqrt{n}$$

at large n , and therefore $x_n \sim -n\Delta x$ to leading order. Thus:

$$\Delta U(x_n) = U(x_n) - U(x_{n-1}) = K \left(n - \frac{1}{2} \right) (\Delta x)^2 - W(x_n) \sim Kn(\Delta x)^2 - W(x_n), \quad (10)$$

$$\Delta U(x_{n+1}) = U(x_{n+1}) - U(x_n) = K \left(n + \frac{1}{2} \right) (\Delta x)^2 - W(x_{n+1}) \sim Kn(\Delta x)^2 - W(x_{n+1}). \quad (11)$$

Let us substitute Equations (10) and (11) into Equation (9) and average the obtained equation. Assuming the independence of C_n^\pm on $W(x_n)$ and taking $\langle C_n^\pm \rangle = \bar{C}$, we find:

$$\langle v_n \rangle \sim \tilde{C} \sinh \left[\frac{Kn(\Delta x)^2}{kT} \right], \quad (12)$$

where:

$$\tilde{C} = 4\bar{C}\Delta x \exp \left[-\frac{\bar{W}}{kT} + \frac{1}{2} \left(\frac{\Sigma}{kT} \right)^2 \right]. \quad (13)$$

Here we have used the relation:

$$\left\langle \exp \left(-\frac{\Delta W_n}{kT} \right) \right\rangle = \exp \left[\frac{\Sigma^2}{2(kT)^2} \right],$$

which is valid for a Gaussian process.

Assuming that Δx is small and $n \gg 1$, we introduce the continuous *macroscopic* coordinate $X = -n\Delta x$ of the particle's center of mass and obtain the following macroscopic evolution equation governing the continuous averaged motion of the particle:

$$\frac{dX}{dt} = -\tilde{C} \sinh(\alpha X), \quad X < 0, \quad (14)$$

where:

$$\alpha = \frac{K\Delta x}{kT}.$$

Solving Equation (14) with a definite initial condition $X(0) = X_0 < 0$, we find that:

$$X(t) = \frac{2}{\alpha} \tanh^{-1} \left[\tanh \left(\frac{\alpha X_0}{2} \right) \exp(-\tilde{C}at) \right]. \quad (15)$$

For $|X| \gg 1/\alpha$, we can use the asymptotic approximation:

$$\tanh z \sim -1 + 2e^{2z},$$

and thus we find the approximate formula:

$$X(t) \sim \frac{1}{\alpha} \ln \left\{ \left[1 + (-1 + 2 \exp(\alpha X_0)) e^{-\tilde{C}at} \right] / 2 \right\}. \quad (16)$$

In the region $\tilde{C}\alpha t \ll 1$, Equation (16) can be written as

$$X(t) \sim \frac{1}{\alpha} \ln \left[\exp(\alpha X_0) + \frac{1}{2} \tilde{C}\alpha t \right],$$

and hence the evolution is logarithmic. At the final stage of the evolution, when: $\tilde{C}\alpha t \gg 1$,

$$X(t) \sim -\frac{1}{2\alpha} e^{-\tilde{C}\alpha t},$$

i.e., the particle position tends to its final value, $X = 0$, in an exponential way, as in the deterministic case. The transition from the logarithmic to exponential evolution law was formerly predicted in Reference [22] in the case of a periodic potential.

4. Discussion

The logarithmic law obtained for the equilibration of colloidal particles adsorbed at a liquid/gas interface, at first glance, looks similar to the anomalous diffusion of Brownian particles in a random environment, which is mentioned in the introduction. However, the evolution law is different from those predicted in Reference [15,16] in the absence of the parabolic component of the potential. While in the region defined in Equation (4), the spatially irregular force $f(x)$ acting on the particle is of the same order or larger than the regular force $-Kx$, the averaged unidirectional motion law of the particle, according to Equation (12), is determined by the constant K characterizing the regular harmonic potential. The fluctuating part of the potential, $V(x)$, influence only the coefficient, Equation (13), in Equation (12). Therefore, the qualitative behavior of the particle is not sensitive to the details of the irregular component of the potential. That is why it can be reproduced in the framework of the model with a periodic potential, as has been done in Reference [22].

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