Bistability and "Negative" Viscosity for a Suspension of Insulating Particles in an Electric Field

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It is shown that a suspension of insulating particles in a liquid with low conductivity possesses bistability and has a "negative" effective viscosity effect in the electric field due to internal rotations. By Brownian dynamics simulation it has been found that thermal fluctuations of the angular velocity of particles in this bistable system can have a large effect on the viscosity of the suspension.

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The unusual properties of bistable systems in the presence of thermal noise have been of great interest recently [1–4]. Among the properties of these systems we can mention the softening of a mechanical system leading to negative stiffness [1], the negative friction coefficient of the fluctuating bistable systems [2,3], and the negative resistance due to the rectification of Brownian motion [4]. Interesting possibilities for the investigation of the unusual properties of bistable systems offer the assemblies of the particles or drops in the insulating liquids which exhibit the interesting phenomena of agglomeration and spontaneous rotation of the aggregates in the electric field [5–9]. A simple system with bistable behavior arises due to the so-called Von Quincke effect when the spontaneous rotation of the dielectric rod, immersed in an insulating liquid, in one or another direction occurs at a dc electric field strength larger than the threshold value [10]. Intriguing effects caused by spontaneous rotations take place in a suspension of insulating particles. At an electric field strength larger than the threshold value an increase in the conductivity of the suspension due to convective charge transfer has been observed [11]. The orientating effect of macroscopic shear flow on the rotation of particles can produce a spontaneous macroscopic motion of a suspension with a free boundary in an electric field even below the threshold value of the Von Quincke effect [12]. The possibility of sustaining the macroscopic motion of a liquid in a homogeneous electric field without applying any force has been experimentally confirmed [13]. A direct increase of the flow rate of the suspension with insulating particles—a "negative" viscosity effect—has been observed quite recently [14].

The theoretical models of spontaneous rotation phenomena are based on the polarization relaxation equation describing the kinetics of free charge accumulation on the interface of spherical particle due to the difference of electrophysical properties of the media [15] (for a more complex case of ellipsoidal particles, see [16] and the references therein):

$$\frac{d\vec{P}}{dt} = [\vec{\Omega} \times \vec{P}] - \frac{1}{\tau}[\vec{P} - \epsilon_0(\chi_0 - \chi_\infty)\vec{E}]; \qquad (1)$$

$$\vec{\Omega} = \vec{\Omega}_0 + \frac{V}{\alpha}[\vec{P} \times \vec{E}]. \qquad (2)$$

Here $\vec{\Omega}$ is the angular velocity of the particle, $\vec{\Omega}_0$ is the vorticity of a flow, $\alpha = 6\eta V$ is the rotational friction coefficient of a spherical particle with volume V, ϵ_0 is permittivity of free space, $\chi_{0,\infty}$ are susceptibilities of particle polarization at low and high electric field frequencies correspondingly:

$$\chi_0 = 3\epsilon_1 \frac{\gamma_2 - \gamma_1}{\gamma_2 + 2\gamma_1};$$

$$\chi_\infty = 3\epsilon_1 \frac{\epsilon_2 - \epsilon_1}{\epsilon_2 + 2\epsilon_1}.$$

$\tau = \frac{\epsilon_0(\epsilon_2 + 2\epsilon_1)}{(\gamma_2 + 2\gamma_1)}$ is the Maxwell relaxation time, $\epsilon_{1,2}$ and $\gamma_{1,2}$ are, respectively, the relative dielectric permittivity and conductivity, and index 1 refers to the fluid and index 2 to the particle. For a quiescent liquid, if the rotational inertia of a particle is taken into account, the set of equations (1) and (2) coincides with the famous set of Lorentz equations [17], where the following values of parameters are valid (in standard notation): $r = (\frac{E}{E_c})^2$; $\sigma = \frac{\tau}{\tau_r}$; $b = 1$[18]. Here $\tau_r = \frac{I}{\alpha}$ is the characteristic inertial time, I is the moment of inertia of the particle, and $E_c^2 = -\frac{\alpha}{\epsilon_0(\chi_0 - \chi_\infty)\tau V}$ is the threshold value of the critical electric field strength for spontaneous rotations of particles. For spontaneous rotations to occur the condition $\frac{\epsilon_1}{\gamma_1} < \frac{\epsilon_2}{\gamma_2}$ is necessary.

It should be noted that the set of polarization relaxation equations (1) and (2) formally is equivalent to the phenomenological magnetization relaxation equation of magnetic colloids, suggested on a phenomenological basis by Shliomis in 1971 for the description of magnetic relaxation of magnetic dipoles in an external field in the presence of thermal noise [19]. As it turned out later in this case the relaxation equation describes correctly the behavior of a colloid only for small shear rates [20]. The discrepancy is connected with the procedure of the splitting of moments of orientation distribution function which arises at the solution of the Fokker-Planck equation. This is not a case of polarization relaxation equations (1) and (2) which are exactly derived from the equations of electrostatics and charge conservation [15].

The spontaneous rotations arising at $E > E_c$ are degenerate since they can take place in both counterclockwise and clockwise directions:

$$\Omega = \pm\frac{1}{\tau}\sqrt{\frac{E^2}{E_c^2} - 1}.$$

In the flow the degeneracy disappears and bifurcation becomes imperfect [11]. In this situation the thermal fluctuations of particle rotation can be important, since they can change the population probabilities of the two possible states of rotation. These transitions could help us understand the quantitative discrepancy which exists between the predictions of the theoretical model and the experimental data [14]. In this Letter the influence of random thermal fluctuations on a negative viscosity effect has been studied numerically by means of Brownian dynamics [20]. The set of the Langevin equations includes Eq. (1), where the transfer of charge due to the random rotation of a particle is accounted for, and Eq. (2). The equation (1) with a term accounting for the random noise of the particle angular velocity $\vec{\Omega}_r$ reads

$$\frac{d\vec{P}}{dt} = [(\vec{\Omega} + \vec{\Omega}_r) \times \vec{P}] - \frac{1}{\tau}[\vec{P} - \epsilon_0(\chi_0 - \chi_\infty)\vec{E}]. \quad (3)$$

To realize the Brownian dynamics $\vec{P}$ is expressed as $\vec{P} = P\vec{n}$, where $\vec{n}$ is a unit vector along the direction of particle polarization. Then $[P = -\epsilon_0(\chi_0 - \chi_\infty)E\tilde{P}$; $\vec{e}$ is a unit vector in the direction of the electric field; hereafter tildes are omitted]

$$\frac{dP}{dt} = -\frac{1}{\tau}(P + \vec{e}\cdot\vec{n}), \quad (4)$$

$$\frac{d\vec{n}}{dt} = [\vec{\Omega}_n \times \vec{n}]. \quad (5)$$

Here the angular velocity of polarization direction rotation $\vec{\Omega}_n$ is

$$\vec{\Omega}_n = \vec{\Omega}_0 + \vec{\Omega}_r + \frac{1}{\tau P}\left(1 - \frac{E^2}{E_c^2}P^2\right)[\vec{e} \times \vec{n}]. \quad (6)$$

In the case when thermal fluctuations are absent, Eqs. (4) and (6) for $P_y = -n_y n_z$ in the steady case give ($\vec{\Omega}_0 = \Omega_0 \vec{e}_x$)

$$P_y\left(1 - \frac{E^2}{E_c^2} + (\Omega_0\tau)^2\right) + 2\Omega_0\tau\frac{E^2}{E_c^2}P_y^2 + \left(\frac{E^2}{E_c^2}\right)^2 P_y^3 - \Omega_0\tau = 0. \quad (7)$$

The solutions of Eq. (7) for $\frac{E^2}{E_c^2} = 2$ as function of $\Omega_0\tau$ are shown in Fig. 1. It can be seen that, in a certain range of vorticity that depends on the strength of the electric field, Eq. (7) has three solutions, one of which, illustrated by curve 2 in Fig. 1, is unstable. The two solutions shown by curves 1 and 3 correspond to the negative and positive viscosity effects. Since $n_z > 0$ then solution 3 has $P_y > 0$, but solution 1 $P_y < 0$. This means that on branch 3 the relative rotation of particles occurs in the counterclockwise direction and thus diminishes the effective viscosity. Particles with polarization corresponding to branch 1 have $P_y < 0$ and rotate clockwise relative to the liquid. This leads to an increase in the effective viscosity. Since the system is bistable in the definite range of the shear rate and a contribution of each state to the effective viscosity effect has the opposite sign, there is a strong effect of the thermal fluctuations. For its calculation, according to the method of Brownian dynamics, the macroscopic values of the polarization are found by means of averaging along the Brownian trajectory of the particle. To realize Brownian dynamics the moving orthonormal frame $\{\vec{e}_1, \vec{e}_2, \vec{e}_3\}$ is introduced. Here $\vec{e}_1 = [\vec{n}_0 \times \vec{e}]/|[\vec{n}_0 \times \vec{e}]|$; $\vec{e}_2 = [\vec{n}_0 \times \vec{e}_1]$; $\vec{e}_3 = \vec{n}_0$, but $\vec{n}_0$ is the instantaneous value of $\vec{n}$. The variations of components of the vector $\vec{n}$ during the time step Δt are expressed as follows:

$$\Delta n_1 = \Omega_{n2}\Delta t; \qquad \Delta n_2 = -\Omega_{n1}\Delta t,$$

but the component along $\vec{e}_3$ is found from the conservation of the length of the unit vector $\vec{n}$. Because of the fluctuation-dissipation theorem the random angles of rotation $\Omega_{1r}\Delta t$ and $\Omega_{2r}\Delta t$ are distributed according to the Gaussian law with a zero mean value and a dispersion $\frac{2k_BT}{\alpha}\Delta t$. After each time step the components of the vector $\vec{n}$ in the laboratory set of coordinates are found according to the relations given in [20,21]. For a qualitative illustration of what is happening with the present system in the condition of bistability in Figs. 2 and 3 the distributions of $P\vec{n}$ values projected on the yz plane for $4.10^5\tau_B$ long runs with time step $2.10^{-3}\tau_B$ are shown at $\frac{E^2}{E_c^2} = 2$ and $\Omega_0\tau = 0.03$, when, according to results in Fig. 1, the system is bistable. We see that an increase of the ratio of the Brownian and Maxwell relaxation times $\frac{2\tau_B}{\tau}$ changes the occupation probabilities near both stationary states of a bistable system. The equilibration of occupancy probabilities of two states with the counterrotation of particles leads to a considerable decrease of the negative viscosity effect. For the large value of $\frac{2\tau_B}{\tau}$, when thermal fluctuation effects are less expressed, the particle polarization values P_y, P_z in agreement with the curves shown in Fig. 1 are distributed near the state $(+0.5, -0.49)$, which corresponds to the direction of the particle rotation leading to the negative viscosity effect.

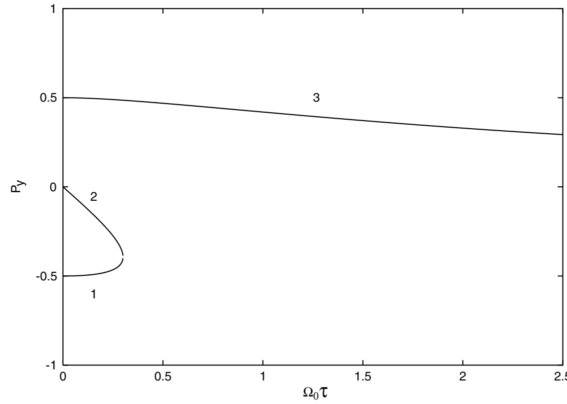

FIG. 1. Solutions of Eq. (7) in dependence on $\Omega_0\tau$; $\frac{E^2}{E_c^2} = 2$.

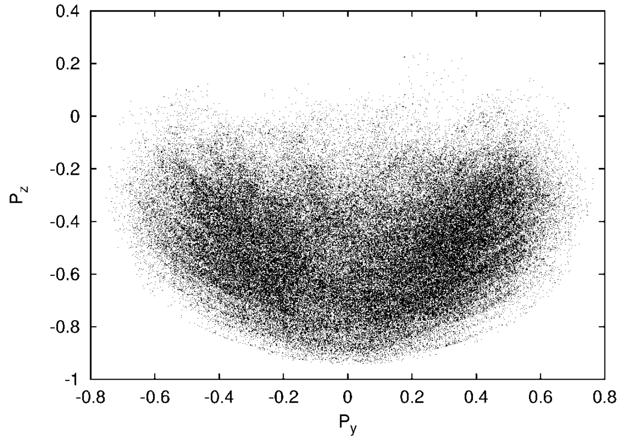

FIG. 2. Probability distribution of the system in phase plane P_y, P_z; $\frac{E^2}{E_c^2} = 2$; $\frac{2\tau_B}{\tau} = 10$. It shows that in the regime of strong fluctuations the probabilities of the polarization values near the steady states, for the given values of the parameters having coordinates $(\pm 0.5; -0.49)$, are practically equal. Thus the "negative" viscosity effect is small in this case since the two populations of particles give the contributions of the opposite sign to the effective viscosity.

The contribution of the rotating particles to the effective viscosity of the suspension is obtained by considering the antisymmetric part of the stress tensor that arises due to the relative rotation of particles with respect to the fluid [19,21]. In the case of a simple shear flow with $\Omega_0 = -\frac{1}{2}\frac{dv_y}{dz}$ and an electric field E in the direction of the z axis, the antisymmetric part of the viscous stress tensor is given by ($\vec{P}^s = nV\vec{P}$ is polarization of the suspension; n is number of particles per volume unit)

$$\sigma_{yz}^a = \tfrac{1}{2} e_{yzx}[\vec{P}^s \times \vec{E}]_x = \tfrac{1}{2} P_y^s E. \tag{8}$$

The contribution of the antisymmetric stress to the effective viscosity of the suspension is given by

$$\frac{\sigma_{yz}^a}{\frac{dv_y}{dz}} = -\frac{n\alpha}{4}\frac{E^2}{E_c^2}\frac{Pn_y}{\Omega_0\tau} = -\frac{n\alpha}{4}\frac{E^2}{E_c^2}\Delta\eta.$$

Since $Pn_y > 0$ at $\Omega_0 > 0$ the particles rotate in the direction imposed by the vorticity; then their contribution to the effective viscosity is negative, the so-called "negative effective viscosity effect" [11–14]. A negative effective viscosity effect, but much weaker and only in ac magnetic fields, is known also for magnetic liquids [22].

The magnitude of the negative viscosity effect in the presence of an electric field, as has been shown by calculations based on the Brownian dynamics, strongly depends on the ratio of characteristic Brownian and Maxwell relaxation times. The absolute values of the contribution of the rotating particles to the effective viscosity of the suspension in dependence on $\omega = \Omega_0\tau$ for different values of $\frac{2\tau_B}{\tau}$ are shown in Fig. 4. It can be seen that the thermalization of particles leads to a considerable decrease of the negative viscosity effect in comparison to the case when the thermal fluctuations are absent.

The negative effective viscosity effect was measured experimentally by the determination of the flow rate through a capillary under the action of an electric field [14]. In the case of the plane Poiseuille flow when $\sigma = -qz$ (σ: tangential stress; $-q$: pressure gradient) the angular velocity of particle rotation Ω is determined by the equation

$$\frac{\tau\sigma}{2\eta} = -\Omega\tau + \left(1 + \frac{n\alpha}{4\eta}\right)\frac{E^2}{E_c^2}\frac{\Omega\tau}{1 + (\Omega\tau)^2}. \tag{9}$$

Above a threshold value of the field strength $E_*^2 = \frac{1}{1 + n\alpha/4\eta}E_c^2$ a spontaneous macroscopic motion of the suspension is possible due to the orientating effect of vorticity [12]. The velocity profile $v_0 f(\tilde{z})$, where $\tilde{z} = z/d$ is a

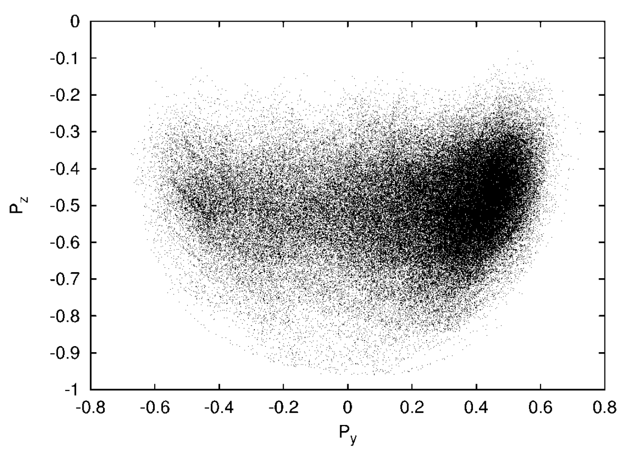

FIG. 3. Probability distribution of the system in phase plane P_y, P_z; $\frac{E^2}{E_c^2} = 2$; $\frac{2\tau_B}{\tau} = 50$. It shows that in the case of weak fluctuations the probability of the polarization value is enhanced near the state with coordinates $(0.5; -0.49)$. This corresponds to the negative viscosity effect. In this case the contribution to the effective viscosity of the particles near the second steady state of a bistable system is small.

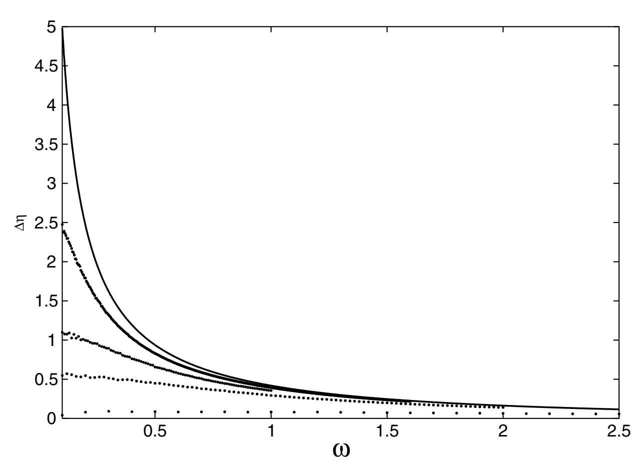

FIG. 4. The negative viscosity effect for different values of $\frac{2\tau_B}{\tau}$ (25; 10; 5; 1) starting from above. The solid line is the theoretical curve for the situation without thermal fluctuations. $\frac{E^2}{E_c^2} = 2$.

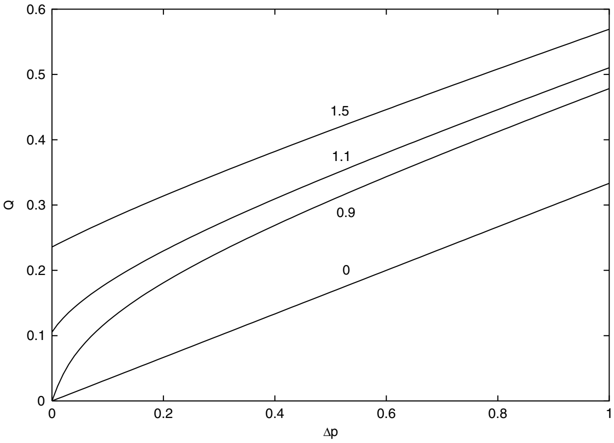

FIG. 5. Flow curves for several values of $\frac{E^2}{E_*^2}$; $a = 2$.

dimensionless coordinate across the capillary and $2d$ is the width of the capillary, is found by integration of the total tangential stress, including the contributions from the shear stress and rotating particles ($a = \frac{n\alpha}{4\eta}$):

$$\frac{\tau}{2d} v_0 f = \frac{\tau q d}{4\eta}(1 - z^2) + \frac{a}{1 + a}\frac{E^2}{E_*^2}\int_z^1 \frac{\Omega_1 \tau}{1 + (\Omega_1 \tau)^2} dz. \quad (10)$$

Here Ω_1 is the corresponding root of the cubic equation (9). In this case since the particles rotate in the directions determined by the vorticity, which are opposite on each side from the symmetry plane of the flow, the shear rate has a jump on the symmetry plane of flow at $\frac{E^2}{E_*^2} > 1$. The particles rotating in opposite directions cause a force in the direction of flow which manifests itself as a diminuition of the viscosity of the suspension.

The flow curves are calculated numerically by integrating the relation (10). The flow curves for several values of the electric field strength are shown in Fig. 5. They are similar to flow curves of Newtonian liquid except that the volume flux is possible at $\frac{E^2}{E_*^2} > 1$ even without a pressure gradient due to spontaneous rotations of particles. This is a pumping effect of the rotating particles. Such effects are used to create pumps for microfluidics [23]. Dimensionless variables Δp and Q in Fig. 5 are scaled with $\frac{2\eta}{\tau d}$ and $\frac{2d^2}{\tau}$ correspondingly. The flow curves in Fig. 5 are qualitatively similar to those observed in the experiment [14]. Nevertheless, there is a certain quantitative mismatch between the experimental flow curves and theoretical ones. In addition to the peculiarities of geometry that cause the inhomogeneity of internal rotations, the effects due to equilibration of occupation probabilities of a bistable system, caused by thermal noise or random hydrodynamic interactions, can also be important. The role of the hydrodynamic interaction of rotating particles in pattern formation of the system of magnetic particles is illustrated in [24]. The thermal fluctuation effects for the system investigated in [14] evidently may be excluded. The Maxwell relaxation time for the carrier liquid with $\gamma_1 = 2 \times 10^{-8}$ s/m, $\epsilon_1 = 3.4$ and the insulating particles with $\epsilon_2 = 2.6\ 2 \times 10^{-3}$ s is much smaller than the Brownian relaxation of quite large particles with the diameter $a = 100\ \mu$m ($\eta = 10$ cP): $\tau_B = 4 \times 10^6$ s. The critical field for a rising of the Von Quincke rotations in this case is $E_c = 9$ kV/cm, which is in the range of electric field strengths used in the experiment [14]. For the system with electrophysical parameters given above the thermal fluctuations of angular velocity of the particles should be important at $\tau_B = 10\tau$ which gives for the diameter of particles 0.1 μm.

To summarize this Letter we can say that a suspension of insulating particles under the action of an electric field gives an interesting example of a bistable system with a negative effective viscosity effect where the thermal fluctuation effects can play a significant role.

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