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Effective surface dilatational viscosity of highly concentrated particle-laden interfaces

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The effective surface dilatational viscosity is calculated of a flat interface separating two immiscible fluids laden with half-immersed monodisperse rigid spherical non-Brownian particles in the limit of high particle concentration. The derivation is based upon the facts that (i) highly concentrated particle arrays in a plane form a hexagonal structure and (ii) the dominant contribution to the viscous dissipation rate arises in the thin gaps between neighboring particles.

I. INTRODUCTION

Colloidal particles can adsorb irreversibly at the interfaces between two fluids [1]. The capability of the adsorbed particles to stabilize emulsions has been known since the early 20th century [2,3]. This property has applications in many industrial sectors, such as food processing [4], biomedicine [5], and the petroleum industry [6].

Fluid interface with a small concentration of the adsorbed particles can be regarded as a two-dimensional (2D) fluid [7]. It is possible to increase surface concentration of particles by either adding new particles to the interface or changing the surface area [8–13]. As the concentration increases, the interface laden with spherical particles undergoes transition to a 2D crystal state [14] with a possible intermediate hexatic phase between liquid and solid phases [15–17]. Further increase in particle concentration results in buckling of the interface [8–13] and allows producing stable nonspherical armored bubbles [18,19].

Highly concentrated particle-laden interfaces have recently received significant attention as the basis of new soft materials with tunable properties. It has been proposed that colloidal microcapsules formed by self-assembly of particles at the interface of emulsion droplets ("colloidosomes") can used as a tool for controlled delivery of drugs, food, and cosmetic supplements [5,20–22]. Nonsticking fluid droplets encapsulated with solid particles ("liquid marbles") have potential applications in sensors, chemical and biological microreactors, and droplet microfluidics [23,24]. Bicontinuous interfacially jammed emulsion gels ("bijels"), a new class of soft materials stabilized solely by colloidal particles, can potentially serve as a cross-flow microreaction medium [25–27]. Porous materials with controlled porosity and pore sizes can be produced by removing fluid from particle-stabilized emulsions [28]. The effectiveness of colloidal particles in stabilizing emulsions ("Pickering emulsions") also depends on the formation of a sufficiently dense layer of particles at the fluid interface [29].

The surface rheology of particle-laden interfaces is an important factor in the stability of particle-laden films, emulsions, and foams, as well as in their kinetics, such as break-up and coalescence [30,31]. We may expect the surface rheology to play an even larger role at larger particle concentrations, when the gaps between particles are small but not zero. Knowledge of interfacial rheology in this regime may be important for design of efficient manufacturing procedure of the materials based on jammed particle-laden interfaces, mentioned above,

from the lower-concentration particle-laden systems, or for the prediction of their viscoelastic properties. This motivates study of the rheology of highly concentrated particle-laden interfaces.

At sufficiently high concentrations the particle-laden interfaces exhibit viscoelastic behavior [29,32]. Generally viscous and elastic contributions to the surface stress can be separated [33]. A particle-laden interface at large scale can be regarded as continuous, described, in particular, by the effective surface viscosities [34].

For isotropic interfaces the viscous contribution is well described by a Boussinesq-Scriven model with surface shear and dilatational viscosities as the material properties [35]. Isotropic change in the surface area results in a purely dilatational surface flow with the surface velocity field

$$\mathbf{v}_s = \alpha \mathbf{r}, \tag{1}$$

where α is the dilatation rate. The corresponding rate-of-strain tensor is isotropic,

$$\mathsf{S} = \alpha \mathsf{I}_s, \tag{2}$$

where I_s is the surface unit tensor. In this case the viscous contribution to the surface stress tensor, $\boldsymbol{\sigma}_v = \zeta_s \mathsf{S}$, contains a single material parameter, dilatational viscosity ζ_s.

The origin of excess dissipation in particle-laden interfaces lies in modification by the particles of the flow in the bulk fluids that surround the interface. In the extreme case of small concentration of the adsorbed particles the interaction between particles is small, and the interface is purely viscous. In this limit it is possible to calculate effective surface dilatational viscosity of the fluid interface laden with half-immersed monodisperse spherical particles [34]:

$$\zeta_s = 5(\eta_1 + \eta_2)R\phi, \tag{3}$$

where η_1 and η_2 are shear viscosities of the surrounding bulk fluids, R is the radius of the adsorbed particles, and

$$\phi = \frac{\pi R^2 N}{A} \tag{4}$$

is the surface concentration of the particles, with N being the number of particles in surface area A.

In this work the result is presented for the calculation of the effective surface dilatational viscosity in the opposite case of large particle concentrations, which complements the low-concentration result given by Eq. (3).
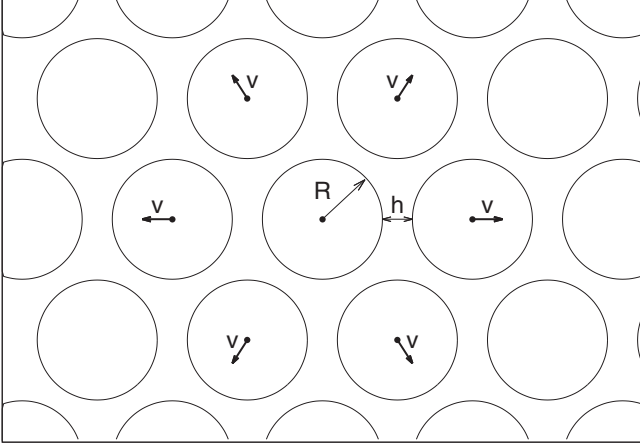
FIG. 1. Hexagonal lattice of spherical particles under dilatational flow.

II. DERIVATION OF THE RESULT

We consider a system of identical rigid spherical particles of radius R adsorbed at the flat interface between two incompressible fluids. We neglect gravity and assume that the interfacial tensions favor a contact angle $\pi/2$, so that the particles are located with the equator coinciding with the interfacial plane.

Different types of interaction between particles trapped at fluid interfaces are possible [36]. We consider the case when the effective interaction between the particles is repulsive, so that they do not agglomerate and the system remains homogeneous. The densest packing of circles in the plane is the hexagonal (honeycomb) lattice, which has packing density

$$\phi_m = \frac{\pi}{2\sqrt{3}}. \tag{5}$$

We consider a large surface concentration of the adsorbed particles, given by Eq. (4), and assume that they are arranged in a hexagonal lattice as shown in Fig. 1. The gap between the particles' surfaces, h, is expressed in terms of the surface concentration of the particles, ϕ, by

$$\frac{1}{h} = \frac{1}{2R}\left(\frac{\sqrt{\phi/\phi_m}}{1 - \sqrt{\phi/\phi_m}}\right). \tag{6}$$

We consider the system being subjected to the flow such that the surface flow field, if unperturbed by particles, would be purely dilatational, given by Eq. (1). Due to symmetry of the system, the neighboring particles move with respect to each other with relative velocity

$$v = \alpha(2R + h), \tag{7}$$

shown in Fig. 1. We assume the interface to be macroscopically thin, having a surface tension sufficiently large to keep the fluid interface flat in the flow.

Frankel and Acrivos [37] established that in highly concentrated three-dimensional suspensions subjected to shear flow the dominant contribution to the viscous dissipation rate comes from the gaps between neighboring particles. They found that the asymptotic rate of viscous dissipation in the fluid with shear viscosity η between two spheres approaching each other

with relative velocity v is given by

$$\dot{E} = \frac{3\pi}{4}\eta v^2 R \frac{R}{h} + O\left(\ln\left(\frac{h}{R}\right)\right). \tag{8}$$

The derivation was based on the exact solution of Stokes equations by Brenner [38]. Further terms in expansion (8) can be obtained using the asymptotic expansion of lubrication force given by Jeffrey [39].

We consider the system with a flat particle-laden interface which is symmetric with respect to the interfacial plane $z = 0$. If shear viscosities of both bulk fluids are equal, the presence of the interface between two bulk fluids does not change the solution of the hydrodynamic equations by Brenner [38] provided surface tangential stress is negligible. This condition is satisfied if there is no additional adsorbed species at the interface, such as surfactants. In the case of different viscosities there is a stress jump across the interface. It is straightforward to show that the tangential traction at the interface equals zero for the flow symmetric with respect to the axis that joins the centers of two particles. The normal traction due to the pressure jump is compensated by surface tension if it is strong enough, so that the interface remains flat. For this to occur, the Laplace pressure,

$$p_L \sim \frac{\sigma}{R}, \tag{9}$$

σ being surface tension, must be large compared to the pressure difference at the interface between two fluids. In lubrication flow the excess pressure in the fluid is of order $\eta v R/h^2$, yielding the pressure jump

$$p_{\text{flow}} \sim \frac{|\eta_1 - \eta_2||\alpha|R^2}{h^2}. \tag{10}$$

The condition $p_L \gg p_{\text{flow}}$ can be cast in the form

$$|\alpha| \ll \frac{\sigma h^2}{|\eta_1 - \eta_2|R^3}, \tag{11}$$

meaning that the interface is flat if the dilatation rate α is small enough. This condition is satisfied in most practical situations involving colloidal particles.

Thus, if condition (11) is satisfied, there is no additional traction due to the presence of the interface between the fluids. As a result, the velocity field remains the same as for the one-fluid problem without the interface. Viscous dissipation in the domain occupied by each bulk fluid will be proportional to the value of corresponding shear viscosity. Therefore, the asymptotic rate of viscous dissipation in the system can be written as a sum of the contributions from each bulk fluid,

$$\dot{E} = \frac{3\pi}{8}(\eta_1 + \eta_2)\frac{v^2 R^2}{h}. \tag{12}$$

In order to calculate the effective dilatational viscosity we shall follow the approach pioneered by Einstein [40] and equate expressions for the rate of viscous dissipation calculated in two ways. First, we consider the system as homogeneous, having an effective continuum interface with effective surface dilatational viscosity ζ_s. Second, we consider the energy dissipation in presence of particles explicitly.

The energy dissipation rate due to dilatational surface flow in a homogeneous surface characterized by dilatational
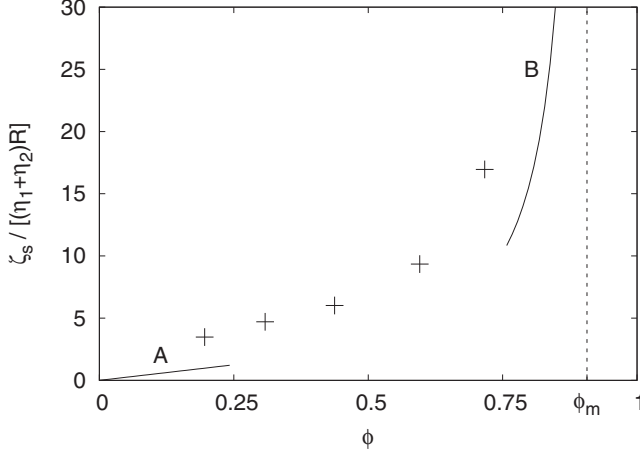
FIG. 2. Asymptotic behavior of dilatational viscosity at low [line A, Eq. (3)] and high [line B, Eq. (18)] particle concentrations. Crosses correspond to the numerical results by Edwards and Wasan [41].

viscosity ζ_s is [35]

$$\dot{E}_h = \zeta_s (\mathrm{Tr}\, \mathsf{S})^2 A, \tag{13}$$

where A is the area of the interface. In our case A equals the area of the hexagonal array of N particles:

$$A = N \frac{\sqrt{3}}{2}(2R + h)^2. \tag{14}$$

Substituting $(\mathrm{Tr}\, \mathsf{S})^2 = 2\alpha^2$ in accordance with Eq. (2), we obtain

$$\dot{E}_h = N\sqrt{3}\,\zeta_s \alpha^2 (2R + h)^2. \tag{15}$$

For dilatational flow in concentrated particle-laden interface we have

$$\dot{E}_p = 3N \frac{3\pi}{8}(\eta_1 + \eta_2)\frac{v^2 R^2}{h}, \tag{16}$$

where $3N$ is a number of lubrication areas between N hexagonally arranged particles. Substituting Eqs. (5), (6), and (7) yields

$$\dot{E}_p = N \frac{9\pi}{16}(\eta_1 + \eta_2)\alpha^2 R(2R + h)^2 \left(\frac{\sqrt{\phi/\phi_m}}{1 - \sqrt{\phi/\phi_m}}\right). \tag{17}$$

Equating two expressions for the energy dissipation rate, (6) and (17), we finally obtain the formula for the effective dilatational viscosity at a large concentration of particles,

$$\zeta_s = \frac{3\sqrt{3}\pi(\eta_1 + \eta_2)R}{16(\sqrt{\phi_m/\phi} - 1)}. \tag{18}$$

This result, together with the low-concentration asymptotics given by Eq. (3), is plotted in Fig. 2.

III. DISCUSSION

The derivation presented in the previous section is based on the idea put forward by Frankel and Acrivos [37], who suggested that fluid flow in the gaps between neighboring particles gives the dominant contribution to the viscous dissipation rate in the highly concentrated suspension, and

they used this idea to calculate the effective shear viscosity of highly concentrated three-dimensional suspensions of solid spherical particles. We shall now discuss possible caveats of this model and their implications on our result.

Frankel and Acrivos considered arrangement of particles in a lattice of fixed geometry. To reconciliate their results with the experimental data, they employed the semiempirical cage model [42] to calculate the viscous dissipation rate and found that the best agreement with the available experimental data is achieved for the cubic arrangement of the particles. However, a condition of fixed particle arrangement is not fulfilled in shear flow and is at best an instantaneous configuration. This fact together with nonuniqueness of the cage model makes the result by Frankel and Acrivos empirical and requires fitting to the experimental data. Returning to our system we note that, in contrast to shear flow, surface dilatational flow conserves hexagonal arrangement of the particles on a surface, so there is no need for empirical parameters in our model.

Berlyand *et al.* [43] considered fluid flow in highly concentrated strictly 2D suspensions and found that in two dimensions different types of singular terms should be considered for adequate description of the divergence of the dissipation rate. In our case this complication does not arise because, although particles are arranged on a 2D plane, fluid flow between them remains three-dimensional. Moreover, of four types of flow considered in Ref. [43], namely, the squeeze, the shear, and two types of rotation, only the squeezing flow, considered in our derivation, is present in purely dilatational flow.

Marrucci and Denn [44] analyzed the result by Frankel and Acrivos and concluded that for the realistic configurations of particles the averaging over relative pair positions of the particles is incorrect, and the models based on regular lattice may present a misleading picture of suspension behavior. In our case the deviation of particles' configuration from a hexagonal lattice also requires separate analysis. However, the presence of the repulsive interaction between particles sufficient to make them non-Brownian removes this, otherwise complicated, problem.

Edwards and Wasan [41] presented the results, shown in Fig. 2, on the effective dilatational viscosity obtained by numerical solution of Stokes equations for the case of adsorbed spherical particles arranged in a square lattice. It is not surprising that the high-concentration results are higher than for hexagonal arrangement of particles because the distance between particles arranged in a square lattice is less. It is less clear why the data at lower concentrations, being larger than predicted by low-concentration formula (3), change slower than proportionally to the particle concentration ϕ.

Estimation of the concentration ranges at which the limiting formulas for the dilatational viscosity, Eqs. (3) and (18), are accurate requires separate investigation. A simple criterium for the applicability of the high-concentration formula (18) can be obtained by requiring viscous dissipation in lubrication gaps between particles to be large compared to the rest of the excess dissipation in the surrounding fluids. This requirement is equivalent to the condition of dilatational analog of the Saffman-Delbrück length [45],

$$l = \frac{\zeta_s}{\eta_1 + \eta_2}, \tag{19}$$

being large compared to the characteristic length for the excess dissipation outside lubrication gaps, which is of order of the particle size R. Expressing Eq. (18) in terms of h and substituting the result in inequality $l \gg R$ yields

$$h \ll \frac{3\sqrt{3}\pi}{8} R \sim R, \qquad (20)$$

which is consistent with the initial assumption that the lubrication gap should be small compared to the size of the particles.

IV. CONCLUSION

We have obtained an asymptotic expression for the effective surface dilatational viscosity of a flat interface separating two immiscible fluids laden with half-immersed monodisperse rigid spherical particles at a high concentration of the particles. The derivation is based upon the facts that (i) highly concentrated particle arrays in a plane form a hexagonal structure, and (ii) the dominant contribution to the viscous dissipation rate arises in the thin gaps between neighboring particles. Dilatational viscosity is given by Eq. (18) and diverges as h^{-1}, where h is the distance between neighboring particles' surfaces.

It should be possible to verify this result by direct experimental measurements. In the case of oscillatory flows the present result, obtained for the case of stationary flow,

represents a low-frequency limit of frequency-dependent dilatational viscosity.

The result can be extended in several ways. It should be possible, with different degrees of complexity, to extend the hydrodynamic model to the cases of different particle shapes, size distributions, different contact angles between the particles and the fluid interface, different curvatures of the interface, combined shear+dilatational flow (e.g., in a Langmuir trough), and so on. If particles adsorbed at the fluid interface are small ("nanoparticles"), physical effects not captured by the simple hydrodynamic model become important and require further investigation, for example, thermal motion of the particles and the interface [46], or modification of fluid viscosity due to confinement [47,48] and viscoelectric [49] effects.

The model for the dilatational viscosity can be used in conjunction with appropriate model for interparticle interactions to describe viscoelasticity of particle-laden interfaces [29]. The present result should allow extending the description of viscoelastic properties to the case of high concentration of the particles.

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