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Plateau-Rayleigh Instability of Ferrofluid Drop-Like Aggregates in Zero Magnetic Field

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Abstract. Experimental investigation was carried out in order to study the properties of drop-like aggregates – the needle-shaped drops of condensed phase, which appear in magnetic fluids undergoing field-induced phase transition of the gas-liquid type. When the applied magnetic field is removed, the needle-shaped aggregates demonstrate the Plateau-Rayleigh instability and disintegrate into series of separate spherical drops due to the surface tension σ at the interface between the gas and liquid phases. The surface tension entirely depends on interparticle interactions, thus experimental investigation of σ allows us to analyse the influence of temperature and magnetic field on the interparticle interactions. It is shown that drop-like aggregates condensed at high temperature demonstrate higher surface tension, than the aggregates condensed at low temperature. This anomalous behaviour can be attributed to the high magnetic field intensity needed to cause the phase transition at high temperature.

1. Introduction

Magnetic fluids (ferrofluids) are stable colloids of magnetic materials in nonmagnetic carrier liquids, which are used in technical applications due to the unique combination of contradictory physical properties: liquid state and high magnetic susceptibility (approx. 1-10 units). Ferrofluids are also widely used for fundamental studies, because they possess exaggerated dipole-dipole interparticle interactions, typical for dipolar media. It is well known, that any gas or liquid containing polar molecules is usually described by a complicated equation of state with numerous virial coefficients [1]. The simplest example of polar fluid is water, because there is no adequate equation of state for water and vapor in all ranges of temperature T and pressure p, which are interesting for technical applications, - and till nowadays the most accurate information about water and its vapor is given in the form of international experimental skeleton tables supplied with approximation fitting equations without any clear physical meaning [2]. Thus it is easier to make fine laboratory measurements and numerical simulations with magnetic fluids [3] than with other polar gases and liquids.

The typical experimental approach to study dipole-dipole interparticle interactions in magnetic fluids is to measure the magnetic susceptibility χ dependence on temperature T and volume concentration φ of particles, because χ is very sensitive to particle interaction and granulometric parameters of the ferrofluid [4, 5]. However there is an alternative way to study interparticle interactions using surface tension σ measurements. This idea comes from the analogy with classic one-component fluids, because in ordinary fluids the phenomenon of surface tension is explained by the energy of intermolecular attraction [1]. It is not excessive to remind the theory of corresponding states by Sugden [6] who suggested to compare molar volumes of liquids at equal surface tension (not at the critical point (T^*, p^*) as it was suggested by Van der Waals), because equal surface tensions guarantee equal intermolecular forces inside the compared samples.

To study the interparticle interactions with σ measurements in ferrofluids we should be able to create the liquid-vapor interface between the gas and liquid phases of colloidal particles: the surface tension at the ferrofluid-air surface is not suitable, of course, because it depends mainly on the interaction of carrier liquid molecules ($\sigma \sim 10^{-3}$ N/m) which exceeds the typical surface tension at the surface of gas-liquid phases of ferroparticles ($\sigma \sim 10^{-7}$-10^{-6} N/m) by 3-4 orders of magnitude. Fortunately, dilute magnetic fluids ($\varphi \sim 0.01$) demonstrate the field-induced first-order phase transition of the "gas-liquid" type under the action of applied magnetic field H. This effect was studied experimentally [7] and numerically [8]. The field-induced phase transition in magnetic fluids resembles phase transition in moist air as the temperature goes down, because the liquid phase condensates in the form of microdroplets (about 1 μm in diameter). The microdroplets grow and coalesce into macroscopic drops, the so-called drop-like aggregates (its length ~ 1 mm). Drop-like aggregates elongate along the magnetic field lines and become needle-shaped (see Fig. 1). The drop-like aggregate surface exhibits the measurable surface tension σ, which in general case is the function of temperature T and applied field H. When the applied field is nonzero, all particles interact with the field and with each other simultaneously, and the measurements of σ depend on both interactions. However, if we are interested in the interparticle interactions only, then we should exclude the applied field and study the behavior of drop-like aggregates in the zero field. When the external field is switched off, the needle-shaped drop-like aggregate disintegrates into series of separate spherical drops due to hydrodynamic Plateau-Rayleigh instability [9-11] (see Fig. 1).

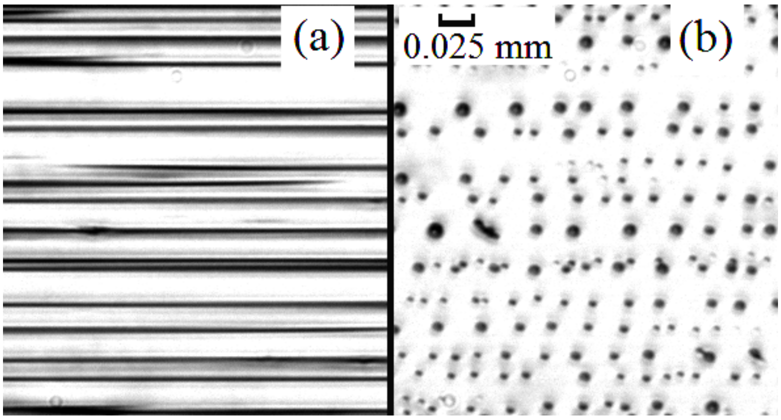

Figure 1. Thin horizontal layer of magnetic fluid with drop-like aggregates condensed during the field-induced phase transition stretch along the H field lines (a) disintegrate into series of separate spherical drops (b) due to the surface tension σ after the applied field is turned to zero.

To sum it up, the present paper delivers new experimental investigation of the surface tension σ at the ferroparticle liquid-gas interface, based on the analysis of Plateau-Rayleigh capillary instability of drop-like aggregates in the zero applied field, while the drop-like aggregates are preliminary condensed by the nonzero field. There is no contradiction between applying the nonzero field H to cause the field-induced phase transition, and removing the field in order to measure σ, which depends entirely on interparticle interactions.

2. Main and auxiliary experimental setups

New experimental setup was made in order to investigate Plateau-Rayleigh capillary instability of drop-like aggregates. The most convincing and simple are the direct visual measurements, that is why it was decided to study drop-like aggregates in a thin horizontal layer (Hele-Shaw cell) placed at the center of Helmholtz coils (Fig. 2). The Hele-Shaw cell was made of two parallel glass plates with a thin square copper wire frame placed between them. The base and the cover glasses were 10.0 mm and 1.3 mm thick, respectively. The wire diameter specified the thickness of the ferrofluid layer (0.2 mm), which was small compared to its length and width (30 mm) and large compared to the diameter of a drop-like aggregate (approx. 0.02 mm). The cell was sealed with hot (120 C) Canada balsam to prevent evaporation of the ferrofluid sample.

The ferrofluid temperature T was controlled by the liquid thermostat (not shown in the Fig. 2). The temperature was measured by two copper-constantan thermocouples. The hot junction of thermocouple TC_1 was embedded in a straight groove on the surface of the Hele-Shaw cell wall and its cold junction was placed in a Dewar flask with melting ice. Both junctions of the thermocouple TC_2 were located in the wall grooves as far from each other as possible. The signal from both thermocouples was simultaneously measured by multichannel 24-bit ADC. Thus, TC_1 measured the temperature of the fluid and the TC_2 measured the temperature inhomogeneity inside the ferrofluid layer. The inaccuracy of temperature measurements did not exceed 0.3 C.

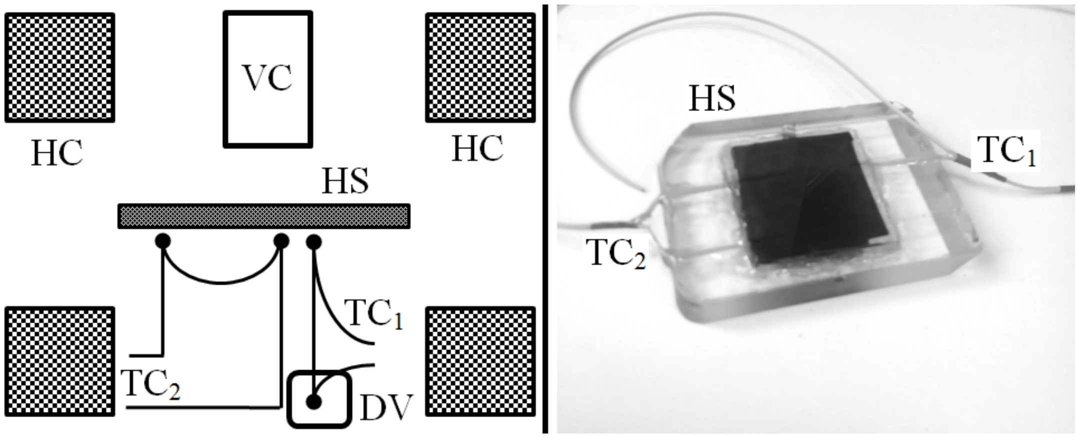

Figure 2. The experimental setup scheme (on the left) and the Hele-Shaw cell (HS) filled with magnetic fluid (on the right): TC – thermocouples, HC – Helmholtz coils, DV – Dewar flask, VC – video camera.

Video camera was integrated in the head of the instrumental microscope. Video camera recorded the disintegration process of drop-like aggregates at given T and use this raw experimental data for numerical analysis of the Plateau-Rayleigh instability. The numerical analysis allowed to calculate σ.

The procedure of experimental measurements was the following. First, the desired temperature T was set on the controls of the liquid thermostat, and after a while (approx. 1 hour) thermocouples registered the thermal equilibrium state of the system "thermostat – measuring cell" (TC_1 readings were steady and TC_2 readings registered temperature inhomogeneity along the cell less than 0.1 C). Second, the Helmholtz coils were powered by stabilized DC power supply in order to generate homogeneous magnetic field. The electric current flowing through the coils was slowly increased till it was enough to cause the first-order phase transition in the magnetic fluid sample. This process was observed on the computer screen attached to the video camera VC (Fig. 2). When the phase transition process was over (it usually took approx. 1 hour) the drop-like aggregates stopped to grow and coalesce. Third, the camera was switched on for recording and the applied field was abruptly switched off (the power source wire was detached). The disintegration process duration varied from several seconds to half a minute. Then the recording was stopped and everything repeated from beginning at the new desired T (however, sometimes it took several hours more to wait till all drops of condensed phase evaporated into the surrounding homogeneous colloid).

The main experiment (Fig. 2) required also the independent auxiliary experiment in order to measure the density and the viscosity temperature dependencies for the gas η_1(T) and liquid η_2(T) phases, because this experimental data is needed for numerical processing. For this purpose drop-like aggregates (the liquid phase) were separated from the surrounding gas phase in the auxiliary setup (Fig. 3(a)).

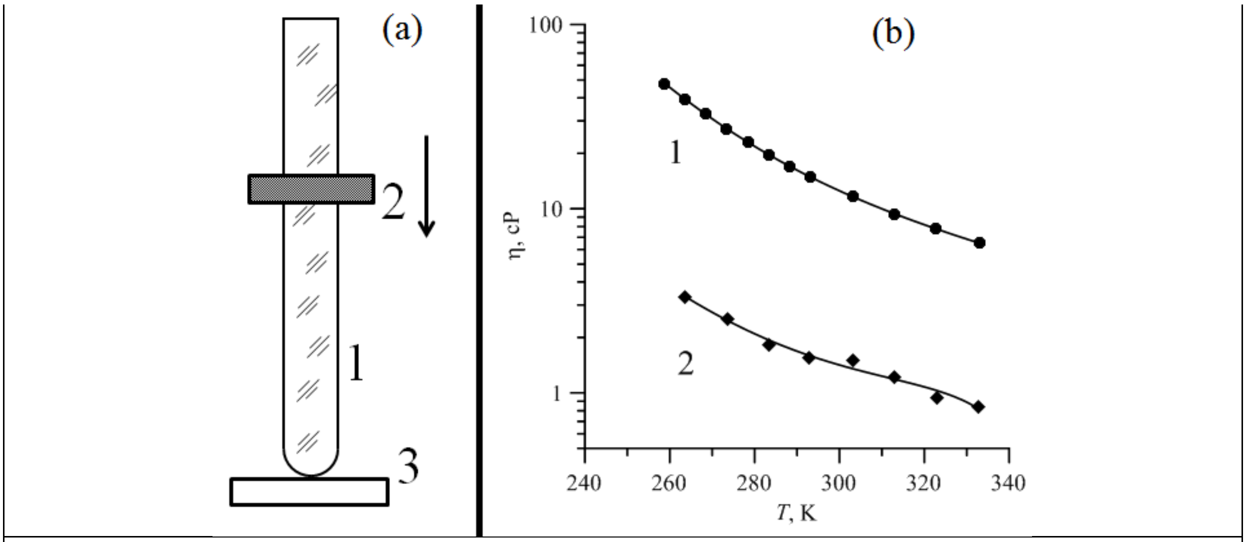

Figure 3. The auxiliary setup (a): 1 - test tube with ferrofluid; 2 - ring magnet collecting drop-like aggregates at the bottom of the tube; 3 - mount plate. The $\eta(T)$ dependence for the liquid and gas phases (curve 1 and 2 on (b) respectively): dots - experiment, solid lines - fitting curves.

The auxiliary setup was used to condensate and collect drop-like aggregates at the center of the ring magnet, which was dragged down the test tube with the original ferrofluid sample. The magnet moved slowly (6 cm per hour) to collect all amount of liquid phase at the bottom of the test tube and to avoid the hydrodynamic mixing of phases during sedimentation. The auxiliary setup allowed to collect the required amount of the liquid phase (5 ml) for Brookfield viscometer viscosity measurements (Fig 3(b)).

3. Calculation procedure

Video records (described in the previous section) supplied us with the raw experimental data at each given T for several (5-10) aggregates in the ensemble: the radius (half thickness) of the aggregate before disintegration R_0, the increment τ of perturbations of the aggregate surface $R(t) \sim \exp(t/\tau)$ and the average distance λ between separate drops after the disintegration process (Fig. 1(b)). The characteristic time τ and the characteristic distance λ are the temporal and spatial characteristics of the disintegration process, which are related by the functional dependence known as the dispersion equation [9]. However, the dispersion equation relates not the τ and λ values, but the temporal and spatial frequencies (characterized by the circular frequency ω and the wave number k) of the capillary waves (disturbances) on the surface of the drop-like aggregate. In the general case the disintegration process is oscillatory and the circular frequency in the dispersion equation $\omega = \omega(k)$ is complex $\omega = \mathrm{Re}(\omega) + i\,\mathrm{Im}(\omega)$, where $i = (-1)^{0.5}$. In our case disintegration is a relaxation (non-periodic) process, therefore the real part of ω equals zero $\mathrm{Re}(\omega) = 0$, and its imaginary part equals the characteristic relaxation time $\mathrm{Im}(\omega) = 1/\tau$.

It is interesting to recall that Chandrasekhar [10] also derived the dispersion equation, but his expression differs from the one obtained by Rayleigh [9], because Rayleigh used the "mechanics" approach that implies complex ω and real k, while Chandrasekhar used the "electrodynamics" approach with real ω and complex k. Probably this difference can be attributed, on the one hand, to the possibility of direct measurements of λ in mechanics, and, on the other hand, to the possibility of generating the electric oscillations of fixed frequency by a signal generator in the XXth century. It is also remarkable that the equivalence of equations published a century (Rayleigh) and half a century (Chandrasekhar) ago was demonstrated (and proved) only in 2018 [11]. However, the Rayleigh theory is too simple for the current study, because it neglects the influence of the surrounding media on the instability of the liquid thread. The appropriate dispersion equation $\omega = \omega(k)$ for the viscous liquid jet (drop-like aggregate) of the radius R_0 surrounded by another viscous immiscible fluid with the surface tension $\sigma(T)$ at the interface was derived in [12] from the zero determinant of the 4x4 matrix with functional elements. It is very complicated, thus it is not given in this paper, because it fully repeats the main result described in [12].

Let us now describe the calculation procedure, which was used to calculate the $\sigma(T)$ dependence. At each given T the central area of the Hele-Shaw cell was captured on video, which was then processed frame-by-frame in the image processing Comef OEG software in order to measure the disintegration of drop-like aggregates. The raw experimental data for each aggregate in the ensemble included the initial radius R_0, the wave-length $k = 2\pi\lambda$ calculated according to the averaged drop-to-drop distance, and $\mathrm{Im}(\omega) = 1/\tau$. The relaxation time τ for each aggregate was found according to the linear theory of the Plateau-Rayleigh instability, which defines the radius of the instable drop-like aggregate $R(t,z)$ as $R(t, z) = R_0(1 + \varepsilon\exp(\mathrm{i}\omega t - \mathrm{i}kz\}))$, where z is the axis parallel to the major axis of the aggregate, ε is the arbitrary initial amplitude of the capillary wave at time $t = 0$, when H is switched off. The direct measurements of the anti-node amplitude (maximum radius R at time t) allows us to calculate τ.

After accomplishing the data preparation procedure, the experimental data for each aggregate was substituted into dispersion equation [12], which was then solved numerically using the Wolfram Matematica package similar to [11]. The final result values of $\sigma(T)$ averaged over an ensemble of aggregates at a given T are present in Fig. 4. Error bars in Fig. 4 are equal to the standard deviation, because all other measurement uncertainties are at least one order of magnitude less.

4. Results and discussions

The experimental study of $\sigma(T)$ described in this paper was carried out to investigate the Plateau-Rayleigh instability of the gas-liquid interface in a zero field. This instability was observed at the surface of drop-like aggregates elongated along the magnetic field lines, which disintegrated into series of separate drops after the applied magnetic field was switched off. The result measurements of $\sigma(T)$ show that the interparticle interactions in the condensed phase demonstrate the nonmonotonous temperature T dependence.

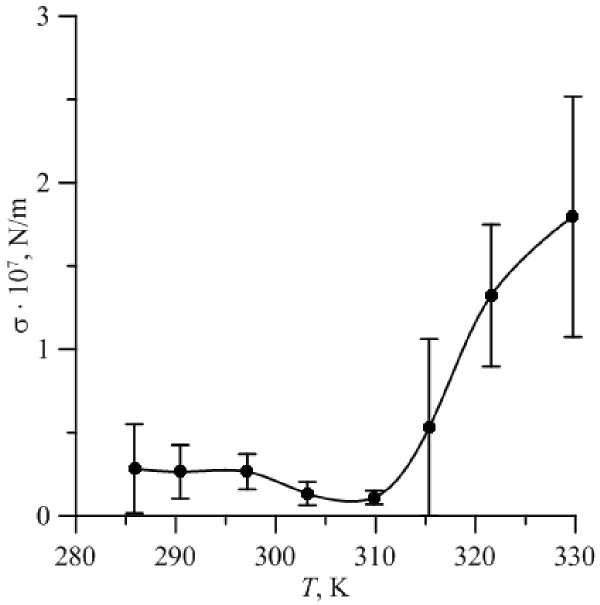

Figure 4. The experimental $\sigma(T)$ curve: dots - experiment, solid line - fitting curve.

The explanation of this anomalous phenomenon may be given in the framework of the Stockmayer fluid model [13], [14]. Thus, the fresh result [14] obtained by means of molecular-dynamics simulations is the following: the applied field H shifts the critical point and interfacial properties σ in different directions, e.g. an external field H parallel to the interface increases the critical temperature. This is actually what happens in our case: the most of drop-like aggregate's surface is parallel to the magnetic field lines, and we can observe the growth of interparticle interactions inside the aggregate, i.e. the increase of σ.

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Another explanation of the observed phenomenon can be given by statistical thermodynamic methods developed in the framework of the molecular theories of liquids [1], [15]. This approach in case of ferrofluids gives the following power dependence $\sigma \sim (\rho_2 - \rho_1)^2$, where ρ_2 and ρ_1 are the mass densities of the liquid and gas phases, respectively. This power-law dependence of σ resembles classical experimental result for one-component fluids $\sigma \sim (\rho_2 - \rho_1)^4$ [16] and is in good qualitative agreement with the Zeldovich theory of surface tension at the interface between two mutually soluble fluids $\sigma \sim (\nabla\rho)^2$ [17]. The work [13] gives us the results of computer simulations of the Stockmayer fluid undergoing the field-induced phase transition, including the densities ρ_2 and ρ_1 at different T and H. As one can see, the density difference $(\rho_2 - \rho_1)$ [13] increases with increase of H and decreases with the increase of T. It means that the final result – the ordinary decrease or anomalous increase of $\sigma(H,T)$ depends on the order (magnetic condensation) -- disorder (thermal motion) competition in the colloid. Thus, the Stockmayer model gives a qualitative explanation of the experimental observations.

5. Conclusions

New experimental investigation was carried out in order to study the properties of the condensed phase drops, which appear in magnetic fluids undergoing field-induced phase transition of the gas-liquid type. When the applied magnetic field is removed, the needle-shaped drops demonstrate the Plateau-Rayleigh instability and disintegrate into series of separate spherical drops due to the surface tension σ at the interface between the gas and liquid phases. The surface tension entirely depends on interparticle interactions, thus experimental investigation of σ allows us to analyse the influence of temperature and magnetic field on the interparticle interactions. It is shown that drop-like aggregates condensed at high temperature demonstrate higher surface tension, than the aggregates condensed at low temperature. This anomalous behaviour can be attributed to the high magnetic field intensity needed to cause the phase transition at high temperature. This phenomenon indicates the increase of interparticle interactions inside the condensed phase with increase of temperature due to the simultaneous increase of the applied magnetic field needed to cause the phase transition.

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