Experimental Evidence of the Motion of a Single Out-of-Equilibrium Drop

Dafne Molin, Roberto Mauri,* and Vincenzo Tricoli

Department of Chemical Engineering, Industrial Chemistry and Material Science, Università di Pisa, 56126 Pisa, Italy

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We show experimentally that when a single, neutrally buoyant drop is injected into a binary mixture either it remains quiescent or it moves, depending on whether the composition of the drop and that of the surrounding phase coincide with the equilibrium concentrations. In general, the movement of out-of-equilibrium drops, which is called diffusiophoresis, is induced by the Korteweg body force. This force is proportional to the chemical potential gradient and is therefore nonzero only when the system is in chemical nonequilibrium. In this letter, we show experimentally that this movement occurs for a single drop as well, even when the initial condition is (almost) isotropic. This instability, although it does not have a complete analytical explanation, has been predicted in the numerical simulations by Vladimirova et al. (Vladimirova, N.; Malagoli, A.; Mauri, R. Phys. Rev. E 1999, 60, 2037-2044).

Introduction


Theoretically, phase transitions in fluid mixtures have been successfully described through the diffuse interface model, also known as the H model under the taxonomy of Hohenberg and Halperin. Here, mass and momentum transports are coupled via a Korteweg body force. This force, which arises from minimizing the free energy of the system, is proportional to chemical potential gradients; therefore, it is identically zero at thermodynamic equilibrium. As shown in many simulations, the Korteweg body force is responsible for diffusiophoresis, that is, the strong motion of the single-phase domains that is observed experimentally during the liquid—liquid phase transition. As expected, when the system is composed of single-phase domains separated by sharp interfaces, the Korteweg body force reduces to the more conventional Marangoni capillary force. By imposing the condition that such a nonequilibrium capillary force balances viscous forces (assuming that inertial forces are negligible), Sicigia showed that the enhanced coalescence caused by such effects can explain the experimentally observed linear growth of the nucleating droplet size during phase separation.

In related works, Karpov and Karpov and Oktoby noticed that capillary forces drive the motion of nucleating droplets along a composition gradient, leading to particle clustering and direct coalescence. A similar phenomenon was also observed by Santonicola et al.,22 who noticed that convection starts to occur as soon as the temperature of the mixture reaches its critical value, well before the appearance of nucleating droplets.

Here we are interested in the motion of a single drop under conditions of nonequilibrium. Such a phenomenon has been studied in other contexts as well. In particular, Kogi et al. studied the behavior of a single micrometer-sized oil droplet that forms at the end of a capillary tube and is immersed in an aqueous surfactant solution. The drop appears to vibrate, with oscillation frequencies and amplitudes that depend on the droplet size and the surfactant concentration. Also, Magome and Yoshikawa studied the self-motion in an oil/water system generated by chemically driven Marangoni instability. This effect was also studied theoretically by Tsemahk et al. In these cases, though,
the movement of the isolated drop arises as a result of uneven surfactant concentration at the interphase during adsorption. As noted above, however, a similar phenomenon can also arise under generic nonequilibrium conditions because of the effects of the Korteweg body force. In fact, numerical simulations by Vladimirova, Malagoli, and Mauri\textsuperscript{1} have shown that a single drop under nonequilibrium conditions is unstable and starts to move, even when the initial configuration is isotropic. In this letter, we intend to document this movement experimentally.

**Experimental Setup and Results**

We employed the acetone–hexadecane mixture that was used in previous work\textsuperscript{26,27} It consists of an isopycnic, partially miscible binary liquid mixture, with the two coexisting phases having the same density, so that buoyancy forces can be neglected. The phase diagram of this binary system is shown in Figure 1. At 20°C, acetone and hexadecane have a $\Delta \rho = 4 \times 10^{-3} \text{g/cm}^3$ (i.e., less than 0.1\%) density difference, and the mixture separates into two phases having 0.25 and 0.80 acetone volume fractions.

The following procedure was utilized in a standard experiment. After a 50/50 acetone–hexadecane mixture was prepared at ambient temperature, we waited for the two phases to separate and then filled a glass tube with the acetone-rich phase. Then, we injected a drop, which was composed of either the hexadecane-rich phase at equilibrium or pure hexadecane. In the first case, the drop was at thermodynamic equilibrium with the surrounding phase, whereas in the second case it was not. The drop was generated and injected using an Eppendorf (CellTram Vario) microinjector, with a capillary tip ranging from 1 to 100 $\mu$m in diameter, so the drop size was in the 10–500 $\mu$m range with a Bond number not exceeding $10^{-5}$. After the injection, the movement of the droplet was monitored from above (i.e., on a horizontal plane) using a CCD camera-video system attached to a Nikon (Eclipse 80i) optical microscope. The experimental setup was designed to avoid vibration of the capillary tip as well as solvent evaporation. All experiments were carried out at room temperature.

Figure 2 shows the typical behavior of a drop at equilibrium with the surrounding phase, using a capillary tip with 10 $\mu$m diameter. As the drop exits the capillary end, it does not move until it is pushed away by a new drop. Clearly, although this behavior was largely expected, because drops and the continuum phase are in equilibrium with each other, it shows that there were no spurious effects, such as buoyancy and thermocapillarity, affecting the results of our experiments. The experiment was repeated with drops ranging from 50 to 500 $\mu$m in diameter, with identical results.

Figure 3 shows the typical behavior of a 20 $\mu$m pure hexadecane drop immersed in the surrounding acetone-rich phase. Here, as soon as it is injected, the drop moves in the horizontal plane, away from the capillary tip. Because gravity is perpendicular to the observation plane, this movement cannot be due to buoyancy, also considering that the Bond number is very small. As the droplet moves, its composition changes, tending to reach equilibrium with the surroundings. Eventually, when equilibrium is attained, the drop stops moving. The experiment was repeated with drops ranging from 10 to 100 $\mu$m in diameter and different out-of-equilibrium compositions, with identical results. A few experiments were also conducted using a water–acetoniitrile–toluene mixture, and similar results were obtained.

A rough estimate shows that 10/100 $\mu$m out-of-equilibrium drops move at speeds exceeding 10 $\mu$m/s. Such velocities do not appear to depend strongly on the drop size, although additional experiments are needed to support such a statement. Because no linear increase in the droplet velocity with drop size was observed, we conclude that the motion of the drop cannot be due to thermocapillary effects induced by nonuniform temperature distributions\textsuperscript{28} thus confirming the conclusion that was previously reached. Accordingly, the observed movement of the isolated out-of-equilibrium drop must result from diffusiophoresis, in agreement with the numerical simulations by Vladimirova et al.\textsuperscript{1} Also, following the dimensional analysis of Gupta...
et al., we see that the Korteweg force $f_K$ is much larger than the adhesive force $f_{adh}$ between the drop and the capillary tip. This result can be obtained by considering that $f_K \approx \sigma R^2/\lambda$, where $\sigma \approx 10$ dyn/cm is the liquid–liquid surface tension, $R \approx 10 \mu m$ is the drop radius, and $\lambda \approx 10^{-2} \mu m$ is the interface thickness, whereas $f_{adh} \approx \sigma_{sl} R$, where $\sigma_{sl} \approx 100$ dyn/cm is the solid–liquid surface tension.

**Conclusions**

The present letter provides experimental evidence that, even in the absence of buoyancy and thermocapillary effects, a single droplet under nonequilibrium conditions can move as a result of a net Korteweg force. This force, resulting from free-energy minimization, is proportional to the chemical potential gradient; therefore, it is identically zero under conditions of thermodynamic equilibrium. On the contrary, under nonequilibrium conditions, the Korteweg force induces an instability that, as predicted in numerical simulations by Vladimirova et al., generates the movement of the drop, even when the initial conditions are isotropic.