Anomalous supercooling in a binary liquid mixture

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(Received 8 January 1979; revised manuscript received 2 July 1979)

The authors have measured the limit of supercooling in a binary mixture of 2-6-lutidine and water an order of magnitude nearer to the critical point than has been possible in previous experiments. This adds to the evidence of enhanced relative supercooling in fluids near the critical point. A recent theoretical prediction of this effect is also reported here.

In dimensionless units supercooling in fluids is observed to increase as the critical temperature is approached,[1-3] contrary to theoretical predictions. The present measurements add data a decade closer to the critical temperature T_c and thereby show that the scaled supercoolings predicted by the Becker-Döring[4] and Langer-Turski[5] theories are too small by an order of magnitude. A new theory proposed by Binder and Stauffer[6] predicts the strongly divergent supercooling that is observed.

The measurements were made on the binary liquid mixture 2,6 lutidine-water[7] (L-W), a system with an inverted coexistence curve,[7] as shown schematically in Fig. 1. The parameters ΔT and δT shown in the figure are the only quantities needed to measure the degree of supercooling. The solid line is the coexistence curve $T_{cx}(x)$, where x is, say, the mole fraction of 2,6-lutidine, and $\Delta T \equiv T_{cx}(x) - T_c$. The hatched line in the figure is the limit of metastability, $T_m(x)$; if a sample is quickly heated through the interval $\delta T = T_m(x) - T_{cx}(x)$, homogeneous nucleation should occur quite suddenly [with very slow heating, the system will follow the coexistence curve $T_{cx}(x)$ to its final state at $T = T_c + \Delta T + \delta T$]. One task of nucleation theory is to calculate δT as a function of x or, equivalently $\delta T/\Delta T$ vs $\epsilon \equiv \Delta T/T_c$.

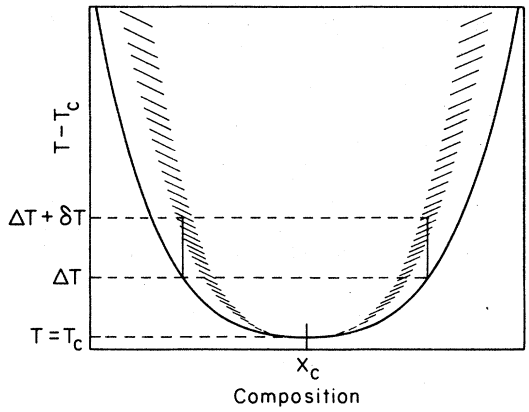

FIG. 1. Phase diagram in the x(composition)-T plane for a system with a lower consolute point. The solid line and hatched line are, respectively, the coexistence curve and metastability limit. x_c is the critical composition.

Experimentally δT was measured by first allowing the sample to come to two-phase equilibrium and then dielectrically heating the mixture to the cloud point by a rapid sequence of microwave pulses. Even though nucleation is induced in L-W by superheating rather than supercooling, we may compare our results with existing theories.[5,6,8]

The experiments suggest that $\delta T/\Delta T$ diverges as $\epsilon \to 0$, as seen in Fig. 2. The theories that predict essentially constant values of $\delta T/\Delta T$ are thus ruled out.

The L-W sample was mixed from commercially available components and sealed under atmospheric pressure in a quartz cell. The cell was of reentrant shape so that most of the observations could be made on that portion of the mixture contained in a disk-shaped region 1.5 mm in diameter and 0.1 mm thick. Nucleation was detected by passing a low-intensity laser beam normal to the disk and noting the temperature at which the intensity I_F of the unscattered beam sharply decreased. The critical temperature of L-W is 33.86 C.[7]

By inverting the cell, the solution could be drained from the reentrant section into a filling tube of 5 mm inside diameter and 3 cm length. This tube served as a convenient place to remix the sample after each run and also to observe nucleation itself, as discussed below.

The experiments were carried out in a temperature-controlled air bath consisting of a Styrofoam box contained within a thick-walled Bakelite box. Coaxial windows permitted entrance and exit of the 6328-Å laser beam and also allowed visual observation of nucleation. The bath stability was ±1 mK over 10 h and ±0.3 mK over 10 min.

The pulsed microwave source was outside the Styrofoam box, but a waveguide inside the Styrofoam box coupled the 15-cm radiation to the sam-

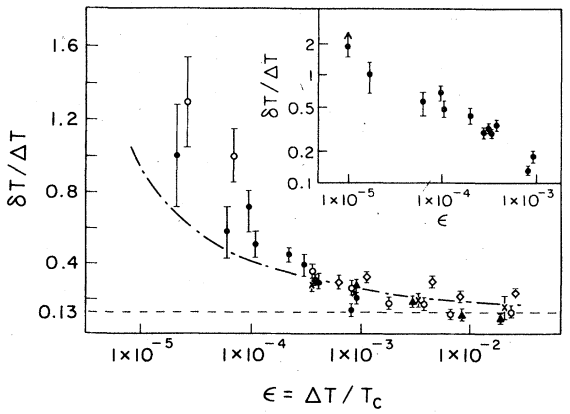

FIG. 2. Supercooling in four fluids. The abscissa is the reduced temperature $\epsilon \equiv |T_c - T_{cx}|/T_c$. The ordinate is the supercooling defined in the units displayed in Fig. 1. The dashed line and the broken line correspond to predictions of Ref. 3, 4, and 6, respectively. The closed (open) circles are the present measurements in the reentrant cell (5-*mm* tube). The data for other fluid systems are from Refs. 1 (◇), 2 (×) and 3 (▲). The insert shows a log-log plot of the reentrant cell data.

ple. This radiation was monitored by a diode placed in its fringing field. The measured dielectric heating rate dT/dt of the mixture was of the order of 10 mK/msec and provided uniform heating of the mixture.[9] The $1/e$ decay time τ_T of a temperature pulse in the mixture was 400 sec.

To obtain accurate measurements of δT one needs the heat capacity c_p, recently measured in L-W.[10] Singular contributions near T_c, as in similar systems,[11,12] are weak. Using the one-phase values of c_p and heating from known initial temperatures up to T_c allows one to relate the integrated microwave power to the resulting temperature rise.

The experiment was performed by allowing the sample, prepared at its critical composition, to equilibrate in the two-phase region at a temperature ΔT above T_c. The mixture was superheated by a series of 10–15 pulses, the last of which produced nucleation. The pulsing lasted less than 30 sec, a time interval small compared to τ_T and the smallest relevant composition diffusion times.[7,13] The measurements were reproducible to within 10%; however, drifts in ΔT increased the errors as T_c was approached.

Figure 2 is a semilog plot of the reduced supercooling as a function of ϵ and shows our own measurements as well as the results of others. The closed circles correspond to measurements in the thin portion of the cell with the laser beam passing through the upper phase, which is rich in 2,6-lutidine. Identical results were obtained in the lower phase. Visual observations confirmed that nucleation occured simultaneously in both phases and was coincident with the drop in I_F.

Suspecting that the above results might be influenced by the small thickness of the reentrant cell, we repeated the entire set of measurements with the sample inverted, so that nucleation took place in the 5-mm stem. These data (open circles) are in an excellent agreement with the thin-cell measurements, implying that wall effects have negligible influence.

The diamonds, triangles, and crosses refer, respectively, to nucleation measurements in C_7H_{14}-C_7F_{14} (Heady and Cahn[1]), CO_2 (Huang, *et al.*[3]), and He^3 (Dahl and Moldover[2]).

All of the data in Fig. 2 are in notable agreement, in spite of the differing methods used to detect nucleation and the disperate thermodynamic properties of the four fluids. The present measurements dramatize the increase in $\delta T/\Delta T$ seen in all of these systems near the critical point because they extend a decade closer to T_c.

The dramatic rise in $\delta T/\Delta T$ as $\epsilon \to 0$ suggests that the data be plotted on a log-log scale. The insert in Fig. 2 is such a plot for the reentrant cell measurements only. In the limited range $-5 \lesssim \log_{10}\epsilon \lesssim -3$, $\delta T/\Delta T \propto \epsilon^{-\phi}$, with $0.5 \leq \phi \leq 1.0$.

The results of several theories are also plotted in Fig. 2. The dashed line represents the B-D theory applied to CO_2.[3] Somewhat improved calculations by Langer and Turski[5] give an almost identical result. The broken line is the Binder-Stauffer result applied to L-W. These authors relate the measured metastability limit $\chi \equiv \delta T/\Delta T$ to the lag time $\tau_{\rm cond}$ for conversion of a fraction f of the mother phase to the daughter phase. The theoretical curve in Fig. 2 was obtained with $f = 1$ and $\tau_{\rm cond} = 1$ sec. This is the approximate interval of observation between successive microwave pulses.

The analysis of Binder and Stauffer leads to the result that for a given ϵ, χ is a decreasing function of τ. Dahl and Moldover report seeing this effect in their He^3 experiments. Their measurements in Fig. 2 correspond to $\tau = 3$ sec, but another set of experiments, for which $\tau = 100$ sec, shows considerably less supercooling. Our observations at $\Delta T = 15$ mK ($\epsilon = 5\times10^{-5}$), show phase separation to occur at $\chi = 0.2$ after a time τ of several minutes, whereas $\chi = 0.6$ when $\tau = 1$ sec. Binder and Stauffer predict that the lag time corresponding to $\chi = 0.2$ is 10^4 sec. For larger τ and small χ, we observe cloudiness first appearing at the interface and then propagating inwards through both phases.

This time-lag phenomenon was further examined by means of a temperature-controlled water bath, so that the thermal equilibration time between sample and bath could be reduced from minutes to

seconds. This time, at relatively small value of δT cloudiness developed uniformly throughout the lower phase, but only after several minutes. In the water bath there was no evidence that nucleation began at the interface. It is possible that delayed nucleation in the air-bath experiment is associated with heterogeneous nucleation which propagates slowly from the interface. The suppression of interface nucleation in the water bath may result from the rapid removal of the (negative) latent heat of nucleation at this surface.[14] It is therefore possible that these lag-time observations in L-W do not as yet test the theory. In CO_2, however, Huang *et al.*[3] held a sample in a metastable state at $\chi = 0.184$ and $\epsilon = 2 \times 10^{-3}$ for 245 min before inducing phase separation. The lifetime predicted[6] at these values of χ and ϵ is of the order of 10 sec. Hence there remains a troublesome disagreement between theory and experiment.

In summary, we have measured the reduced supercooling $\delta T/\Delta T$ as a function of $\epsilon = \Delta T/T_c$ in a critical binary mixture of 2,6-lutidine and water. Near T_c, $\delta T/\Delta T$ increases well above the Becker-Doring limit and may even diverge there with an exponent $\phi \gtrsim 0.5$. Our data lend support to recent theoretical work of Binder and Stauffer which, while not in quantitative agreement with experiment, holds promise for progress in our understanding of nucleation.

We have profited from discussion and correspondence with K. Binder, J. Cohen, Y. C. Chou, R. B. Griffiths, J. S. Huang, M. W. Kim, J. S. Langer, M. R. Moldover, D. Nicole, T. Ohta, J. Thoen, and W. Van Dael. Special thanks are due to Mr. Chou, who carried out the water-bath measurements, and to J. S. Huang and M. W. Kim for their heat-capacity data. This work was supported by the NSF.

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[1]R. B. Heady and J. W. Cahn, J. Chem. Phys. 58, 896 (1973).

[2]David Dahl and M. R. Moldover, Phys. Rev. Lett. 27, 1421 (1971).

[3]J. S. Huang, W. I. Goldburg, and M. R. Moldover, Phys. Rev. Lett. 34, 639 (1975); W. I. Goldburg and J. S. Huang, in *Physics of Nonequilibrium Systems* edited by T. Riste (Plenum, New York, 1975), p. 87.

[4]See, for example, J. Frenkel, *Kinetic Theory of Liquids* (Dover, New York, 1946).

[5]J. S. Langer and L. A. Turski, Phys. Rev. A 8, 3230 (1973).

[6]K. Binder and D. Stauffer, Adv. Phys. 25, 343 (1976).

[7]A. Stein, S. J. Davidson, J. C. Allegra, and G. F. Allen, J. Chem. Phys. 56, 6164 (1972); E. Gulari, A. F. Collings, R. L. Schmidt, and C. J. Pings, *ibid.* 56, 6169 (1972).

[8]See, for example, *Nucleation*, edited by A. C. Zettlemoyer (Dekker, New York, 1969); *Nucleation Phenomena*, edited by A. C. Zettlemoyer (Elsevier, New York, 1977). For a complete list of references, see also K. Binder and M. H. Kalos, J. Statist. Phys. (in press).

[9]Details of this microwave quenching system are to be found in the Ph. D. thesis of Arthur J. Schwartz, University of Pittsburgh, 1978 (unpublished).

[10]M. W. Kim and J. S. Huang (private communications).

[11]A. F. G. Coper, H. H. Reamer, and C. J. Pings, Dtsch. Bunsen Ges. Phys. Chem. Berichte 76, 318 (1972); B. Vishwanathan, K. Govindarajan, and E. S. R. Gopal, Indian J. Pure Appl. Phys. 11, 157 (1973); M. A. Anisimov, A. V. Voronel, and T. M. Ovodova, Sov. Phys. JETP 35, 536 (1972).

[12]J. Thoen, E. Bloemen, and W. Van Dael, J. Chem. Phys. 68, 735 (1978). As theoretically predicted, c_p diverges more strongly in triethylamine-water.

[13]Walter I. Goldburg, Ching-Hao Shaw, John S. Huang, and Michael S. Pilant, J. Chem. Phys. 68, 484 (1978).

[14]In systems with an inverted coexistence curve, nucleation is accompanied by an absorption of heat. This follows from Le Chatelier's principle and from direct calculation [R. B. Griffiths (private communication)].