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Active-coupling mixing times for a stirred binary liquid

C. K. Chan, J. V. Maher, and W. I. Goldburg
Department of Physics, University of Pittsburgh, Pittsburgh, Pennsylvania 15260
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It has previously been reported by Easwar *et al.* that the two phases of a critical mixture take an unexpectedly long time to mutually dissolve if the system is raised above its critical temperature ($T > T_c$) and strongly stirred. Further experiments have identified a trivial explanation for this effect. The system cools on mixing, and this can temporarily drive it back into the two-phase region ($T < T_c$). The experimental technique used here can possibly be exploited to measure the surface energy temporarily stored in a turbulently stirred two-phase system.

In a previous Letter[1] the turbulent mixing of two mutually soluble phases was reported to be anomalously slow near the critical point. We have subsequently discovered the reason for this slow mixing, and it is a trivial one: As the two phases begin to dissolve under stirring, the system cools. This cooling temporarily drives the mixture below its critical temperature (T_c), where phase separation is favored. After sufficient time, heat from the external bath warms the system above its phase separation temperature (T_c), and the phases finally dissolve. The presence of this (negative) heat of mixing thus creates the appearance of anomalous behavior, when in fact, it is unrelated to the "active mixing" effects discussed in the paper. Nevertheless, this phenomenon may hold sufficient theoretical and experimental interest to warrant a brief description of the experiment by which we measured this temporary cooling effect.

In these experiments a mixture of critical composition was initially separated into two phases at a temperature $T_i < T_c$. The two phases were then raised to a temperature $T_2 > T_c$, where they were turbulently mixed by a stirrer within the Pyrex sample cell. During this process the water bath surrounding the sample was held at T_2. After a time τ the phases mutually dissolved and the mixture became clear. A thermometer sealed within the cell has now revealed that mutual dissolution of the phases could cool the sample below T_c. In time, of course, the stirred mixture returns to the bath temperture T_2. This experiment establishes that the mixing time τ of Ref. 1 is equal to the time for the system to warm back through a temperature where the two phases have become mutually soluble under stirring. Once above this temperature, mixing is almost instantaneous.

As expected, if T_2 exceeds some critical value, the negative heat of cooling is too small to drive the system below the critical temperature. In this situation the mixing is observed to be rapid. A reanalysis of our initial measurements and new experiments on another binary mixture (2,6-lutidine-water) are all consistent with the above interpretation. For a system with an inverted coexistence curve (e.g., lutidine-water), the mixing of the phases causes the sample to heat rather than cool on mixing.

A mean-field calculation seems sufficient to explain the effect, since it presumably arises from nonsingular terms in the Helmholtz free energy F. We calculate that the temperature change ΔT_m produced by the mixing is proportional to $[c_c - c(T_i)]^2 \sim |T_c - T_1|^{2\beta}$ if the specific heat of the mixture has negligible temperature dependence. The order parameter here is the concentration c, and the critical exponent $\beta \simeq 0.31$. The term in F responsible for the effect is proportional to T^2 and is independent of $c - c_c$ (there is no contribution from a term in F which is linear in $c - c_c$).

Experimentally we find that ΔT_m is much larger in 3-methylpentane-nitroethane (3MP$-$NE) (Ref. 2) than in lutidine-water, and could slightly influence measurements of phase separation near the critical point. For example, in 3MP$-$NE, $\Delta T \simeq 10$ mK at $T_c - T_i = 30$ mK and 170 mK at $T_c - T_i = 1\,^\circ\mathrm{C}$.

Are there other sources of temperature change produced by turbulent mixing of two phases? Presumably vigorous stirring of a mixture in the two-phase region will produce composition variations of very small spatial extent and costing a correspondingly large surface energy. We estimate this effect to be marginally measurable through the monitoring of a global temperature change in the system as the surfaces disappear after stirring has stopped.

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[1] N. Easwar, J. V. Maher, D. J. Pine, and W. I. Goldburg, Phys. Rev. Lett. 51, 1272 (1983).

[2] G. E. Klinzing, F. J. Aguirre, S. H. Chiang, and W. K. Jing, Chem. Eng. Commun. 17, 117 (1982).