

Active-Coupling Mixing Times for a Stirred Binary Liquid

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Mixing times measured for a stirred critical binary liquid mixture are seen to vary dramatically with Reynolds number, Prandtl number, and the initial value of the order parameter. These variations are far too large to be explained by passive-mixing calculations; they also differ in significant respects from the active-mixing predictions of Ruiz and Nelson.

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Ruiz and Nelson^{1,2} have noted that interesting effects should occur when a binary mixture is strongly stirred near its consolute point. We have observed one of these effects, namely, the anomalously slow rate at which two phases of a turbulent binary mixture mutually dissolve after the mixture is abruptly heated into the one-phase region. This increase in the mixing time presumably arises from the coupling of the velocity of the fluid and the order parameter, which in our case is the local composition. This coupling short circuits the cascade of the composition fluctuations at a relatively small value of wave number $k = k^*$. As a result, the maximum dissolution rate of such fluctuations is retarded, under the assumption that the limiting step is the inverse diffusive relaxation time Dk^{*2} . Here D is the composition diffusion coefficient, which is known to vanish at the critical point (see below).

We observe the increase in mixing time, τ , considered by Ruiz and Nelson (RN) and find it to be orders of magnitude larger than their theory leads one to expect. In the RN approach the force density term in the Navier-Stokes equation that is responsible for the slow down in mixing near the critical point is $-\alpha \nabla^2 \psi \nabla \psi$, where $\alpha (\nabla \psi)^2$ is the usual gradient energy in the Ginzburg-Landau equation. Taking the order parameter, ψ , to be dimensionless, α has the dimensions of ν^2 , where ν is the kinematic viscosity. From an analysis of the coupled equations for fluid flow and diffusion, Ruiz and Nelson predict a so-called active mixing time given by

$$\frac{\tau_{\text{active}}}{t_0} = 1 + \frac{\ln[(\nu^2/\alpha\psi_0^2)\sqrt{R}]}{2\sqrt{R}} + \left(\frac{\alpha\psi_0^2}{\nu^2}\right)\frac{P}{R}, \quad (1)$$

where t_0 is the turnover time (i.e., the inverse frequency) of the stirring force; ψ_0 is the order parameter corresponding to the initial state of the system; R is the stirring Reynolds number; and P is the stirring Prandtl number, ν/D .

In contrast to Eq. (1), passive mixing theories³

set $\alpha = 0$ and predict

$$\frac{\tau_{\text{passive}}}{t_0} = \left(1 + \frac{\ln P}{2\sqrt{R}} + \frac{1}{\sqrt{R}}\right). \quad (2)$$

It is evident that unless the system Prandtl number is unphysically large, the passive mixing time cannot be much larger than t_0 for $R \gg 1$. On the other hand, τ_{active} might substantially exceed t_0 in some physically realizable circumstances because of the linear dependence on P in the third term on the right-hand side of Eq. (1).

In this Letter we report the results of a series of measurements of mixing times for a stirred critical mixture of nitroethane and 3-methylpentane. We have used the known critical properties of this mixture⁴ to achieve high stirring Prandtl numbers and precise control of the initial compositions. In each measurement the system was allowed to phase separate at a temperature $T_i < T_c$ and was then heated to a temperature $T_f > T_c$. Once the system reached thermal equilibrium at T_f , stirring commenced and the mixing time was determined by measuring the intensity of a laser beam transmitted through the sample. The transmitted intensity dropped almost to zero each time the stirring started and then slowly recovered as the two liquid phases mixed. The time required for the intensity to recover to 90% of its final constant value was taken to be the mixing time, τ .

The sample cell shape was roughly that of a right circular cylinder with a vertical axis of symmetry, of height ~ 11 cm and diameter ~ 3.5 cm. The laser beam passed horizontally along a diameter of the cell near the midpoint of its height and about 4 cm above a magnetic stirring propeller of radius 1.2 cm which rotated in the horizontal plane. There was a small but observable delay between the initiation of stirring and the development of apparently homogeneous turbulence in the cell. This time has been carefully measured with the system in the two-phase region; no data are presented herein which have

mixing times less than twice this interval. There were small local heating effects due to the stirring; these were measured and all temperature differences quoted herein have been corrected for the local heating.

The Reynolds number R used in Eqs. (1) and (2) is a stirring Reynolds number, Lv/ν , where L is the stirring propeller radius and $v = 2\pi L/t_0$. Viscosity is known to diverge weakly near the critical point. We have used the known⁴ value of ν at $T_f - T_c = 10$ mK for calculating all Reynolds numbers; the divergence of ν is weak enough to ignore its variation over the temperature range of our measurements. With our stirring apparatus and this definition of R , we have achieved Reynolds numbers $\sim 4 \times 10^4$. Our parameter range of $10^4 \lesssim R \lesssim 4 \times 10^4$ is on the low edge of the range known to show well-developed statistical turbulence with Kolmogorov scaling^{5,6} [Ruiz and Nelson use this scaling idea in deriving Eqs. (1) and (2)]. The local heating rates which we have measured are more than an order of magnitude smaller than would be expected in the limit of Kolmogorov⁷ scaling.

The major results of our measurements are set out in Figs. 1 and 2. Figure 1 shows mixing-time data for a fixed value of ψ_0 and a wide variety of Reynolds numbers and final temperatures, T_f . In this figure the ordinate is the ratio τ/t_0

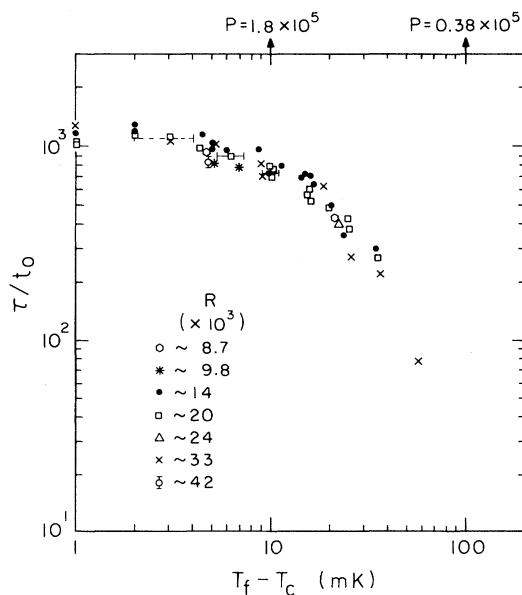


FIG. 1. Mixing time scaled by the turnover time t_0 plotted as a function of $T_f - T_c$, for several different Reynolds numbers. All measurements have $T_c - T_i = 150$ mK. P values are indicated on the upper scale.

$\propto \tau R$. The abscissa is the difference between final (one-phase) temperature and critical temperature, $T_f - T_c$. Since the diffusion coefficient is known to vary as $D(T_f) = D_0[(T_f - T_c)/T_c]^{0.625} = D_0 \epsilon_f^{0.625}$, the abscissa is also equivalent to a reversed Prandtl-number scale and the Prandtl number is indicated on the upper border of the figure. The weak divergence of the viscosity has been included in calculating Prandtl numbers. All the measurements represented in Fig. 1 started with the system at an initial equilibrium temperature 150 mK below T_c . For $T_f - T_c > 50$ mK, the mixing times were always less than twice the time for the fluid in the cell to appear by eye to be fully turbulent. Consequently these data were excluded from the figure.

It is clear from Fig. 1 that τ/t_0 , or equivalently $R\tau$, shows no dependence on R as R is varied by more than a factor of 5. This failure of τ/t_0 to show any R dependence holds true for all initial temperatures, T_i , which we have investigated. Furthermore, τ/t_0 increases strongly and then eventually levels off as $T_f - T_c \rightarrow 0$, and is much larger than 1 for all the data in the figure.

These observations are clearly inconsistent with both Eqs. (1) and (2). In comparing experiment with theory here it must be kept in mind that ψ_0 is a function of the initial temperature difference $T_c - T_i$ and not $T_f - T_c$. For 3-methylpentane + nitroethane, we can combine the equilibrium measurements of others⁴ to obtain the important parameter $\alpha \psi_0^2 / \nu^2 \approx 6.7 \times 10^{-2} \epsilon_i^{2\beta}$ with

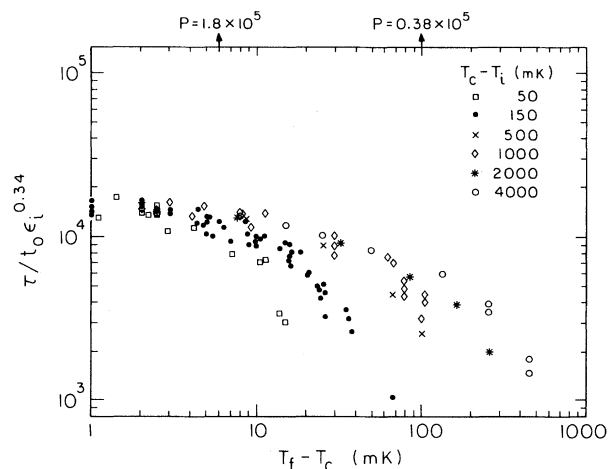


FIG. 2. $\tau/t_0 \epsilon_i^{0.34}$ plotted as a function of $T_f - T_c$. Points are labeled by the initial temperature depth, $T_c - T_i$. Each initial depth includes measurements at various Reynolds numbers. P values are labeled on the upper scale.

$\epsilon_i = (T_c - T_i)/T_c$ and $\beta = 0.34$. With this value the second term on the right-hand side of Eq. (1) is seen to be negligible compared to the third term as long as $R \gg 1$. Then, if P/R is large enough to make the third term $\gg 1$, according to Eq. (1) $\tau/t_0 \epsilon_i^{2\beta}$ should be independent of T_i . No such universality was observed. For example, $\tau/t_0 \epsilon_i^{2\beta}$ evaluated for $T_c - T_i$ equal to 50 and 4000 mK, respectively, differ by as much as a factor of 5. This difference is most pronounced in the temperature regime where P/R is largest, i.e., for T_f near T_c .

On the other hand, we find that the function $\tau/t_0 \epsilon_i^\beta$ is independent of T_i for sufficiently small values of $T_f - T_c$. This can be seen in Fig. 2, which shows the logarithm of $\tau/t_0 \epsilon_i^\beta$ plotted against the logarithm of $T_f - T_c$ for several sets of data. Each of these data sets is characterized by its indicated value of $T_c - T_i$ and each contains measurements for a variety of Reynolds numbers similar to the variations in R shown in Fig. 1. Dividing τ/t_0 by ϵ^β (or equivalently by ψ_0) clearly does not cause all our data to lie on a single curve; each data set shows a different descent from its maximum value. For values of $T_c - T_i \geq 500$ mK all the curves are almost identical, but for $T_c - T_i$ values of 150 and 50 mK the differences are quite pronounced.

Our observations may be summarized by the relation $\tau/t_0 \simeq a \psi_0 f(\epsilon_f, \psi_0)$, where a is a constant and f is a highly nonlinear function which saturates as $\epsilon_f \rightarrow 0$ and falls off steeply from the saturated value as P is reduced below a certain value which depends on ψ_0 .

The leveling off of the reduced mixing time at small values of ϵ_f in Fig. 2 is very likely due to the k dependence of the diffusion constant,⁸ an effect not included by RN. This k dependence should manifest itself when $k^* \xi_f \gtrsim 1$, where ξ_f is the correlation length of the composition fluctuations evaluated at $T = T_f$ (as is well known, ξ diverges rapidly near the critical point⁹). Unfortunately this explanation cannot account for our observation that the flattening occurs at values of $T_f - T_c$ which increase with ψ_0 (see Fig. 2).

In summary, we have seen dramatic variations with Reynolds number, stirring Prandtl number,

and initial order parameter in the mixing times of a stirred binary liquid mixture. These variations are far too large to be explained with passive-mixing calculations and thus presumably arise from active-mixing effects of the sort discussed by Ruiz and Nelson. However, there are several striking discrepancies between our observations and the predictions of Ruiz and Nelson; namely, (1) the failure to observe any Reynolds-number dependence beyond the simple R^{-1} scaling contained in τ/t_0 , (2) the complicated functional dependence on P , (3) the scaling of τ/t_0 with ψ_0 rather than with ψ_0^2 , and (4) the variation in magnitude of τ/t_0 which greatly exceeds reasonable estimates using Eq. (1).

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