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Relaxation of nonequilibrium fluctuations in liquid mixtures above the consolute point

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We study the relaxation of nonequilibrium concentration fluctuations in binary-liquid mixtures near but above the critical consolute temperature. We show that if the strength of the fluctuations is far enough above the thermal level, hydrodynamic effects cause these fluctuations to migrate towards the smallest wave numbers. They are dissipated only in an exceedingly long time at the largest available scale. The structure factor of the fluctuations obeys a scaling law similar to the one observed in experiments of spinodal decomposition. Experimental tests of our result are suggested and their possible relevance to the theory of spinodal decomposition briefly discussed.

I. INTRODUCTION

The dynamics of nonequilibrium fluctuations has been the subject of numerous studies in recent years. In particular, the phenomenon of spinodal decomposition has attracted attention from both theorists and experimenters.[1] After a binary system, like an alloy or a mixture of two liquids, is rapidly cooled into the unstable portion of its phase diagram (see Fig. 1), scattering of light from the system yields a ring pattern that shrinks in time as the decomposition towards the two-phase equilibrium state proceeds. The diameter k_m (in momentum space) of the ring at a given time is proportional to the inverse size of the phase separated regions at that time, and so it gives a measure of the degree of coarsening of the mixture as it phase separates.

To be more quantitative, define $\psi(\vec{r},t)$ as the local departure of the concentration of one of the components of the mixture from its mean value, and let

$$S(\vec{k},t)=\langle\,|\psi(\vec{k},t)|^2\rangle \tag{1.1}$$

be the structure factor. Denoting by $k_m(t)$ the wave number at which $S(\vec{k},t)$ peaks at time t, experiments, both real[1-3] and numerical[4-6] show that $k_m(t)$ has a power-law time dependence,

$$k_m(t)\cong t^{-\phi}\ , \tag{1.2}$$

and that the structure factor obeys a scaling law,[6,7]

$$k_m^3(t)S(k/k_m(t),t)=F(k/k_m)\ , \tag{1.3}$$

the function F being independent of time and of the quench temperature. The exponent ϕ is about $\frac{1}{6}$ for alloys.[1,4,8] For binary liquids at the critical concentration it changes from $\phi\cong\frac{1}{3}$ in the early stages of the decomposition[3,5,8] to $\phi\cong 1$ (Refs. 3 and 9) when the phase separation is well under way.

In this paper we argue that the validity of scaling laws such as (1.2) and (1.3) is not restricted, for liquid mixtures, to evolution at temperatures below the consolute temperature T_c. For instance, if one

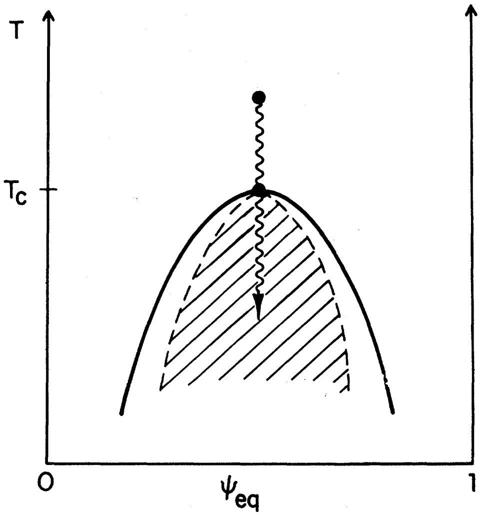

FIG. 1. Schematic plot of the temperature-concentration plane for a symmetric binary mixture. The solid curve bounds the region of two-phase coexistence. Inside the dashed region the concentration susceptiblity is negative. The wavy line illustrates a critical quench.

reverses the quench that brought the mixture into the unstable region, we expect (1.3) to still hold for some time with the same scaling function F, while (1.2) would be obeyed with $\phi \cong \frac{1}{2}$.

The organization of this paper is as follows: In Sec. II we briefly review the basic ingredients entering in the theories of spinodal decomposition and present our derivation of (1.2) and (1.3). In Sec. III we summarize our conclusions and suggest a probably more practical way of experimentally testing our results.

II. DYNAMICAL EQUATIONS

The near-equilibrium dynamics of binary mixtures is fairly well understood.[10,11] A hydrodynamic description of liquid mixtures involves six conserved densities. If we assume the mixture to be incompressible, the two (longitudinal) sound modes decouple from the remaining degrees of freedom. We will, for simplicity, work with the symmetric binary mixture model,[11] in which temperature fluctuations are decoupled from the concentration field $\psi(\vec{r},t)$ which is thus only coupled to the transverse velocity $\vec{v}(\vec{r},t)$. The equations of motion for these three dynamical variables that we retain are[11,12]

$$[\partial_t+\vec{v}(\vec{r},t)\cdot\vec{\nabla}]\psi(\vec{r},t)=\lambda\nabla^2(r_0\psi-\alpha\nabla^2\psi+u\psi^3)+f_\psi\ , \quad (2.1)$$

$$\partial_t\vec{v}(\vec{r},t)=\nu\nabla^2\vec{v}-\alpha\nabla^2\psi\vec{\nabla}\psi+\vec{f}_v\ , \quad (2.2a)$$

$$\vec{\nabla}\cdot\vec{v}(\vec{r},t)=0\ . \quad (2.2b)$$

Here we have taken units in which $k_BT=\rho_0=1$, ρ_0 being the mean density of the liquid. By suitably defining the thermal noises in the right hand sides of (2.1) and (2.2a), it is easy to check that the velocity and the concentration fluctuations relax to the canonical probability distribution associated to the free energy

$$F=\tfrac{1}{2}\int d^3r[\vec{v}^2+\alpha(\vec{\nabla}\psi)^2+r_0\psi^2+\tfrac{1}{2}u\psi^4]\ . \quad (2.3)$$

In the mean-field approximation that we are using, the susceptibility r_0 is negative below the critical temperature T_c. Therefore, just after a temperature quench into the spinodal region has been performed, and if we assume that the term derived from the quartic nonlinearity in (2.3) is negligible, which cannot be a bad approximation in the earliest stages, the right-hand side of (2.1) gives an exponential growth of the concentration fluctuations which is faster around a wave number $k_m=\sqrt{r_0/2\alpha}$. This is basically the idea behind the earliest theories of spinodal decomposition.[2]

Unfortunately, a complete description that includes the subsequent coarsening of the mixture must also include a treatment of the nonlinear terms. Among them, the quartic nonlinearity, required for stability, is by far the most difficult to handle. There are approximate calculations[4,5] that take it into account and agree well with experiments during the early stages of the decomposition,[3] but they are inadequate to describe the latest stages when large regions of different phases are separated by sharp interfacial boundaries. No satisfactory theory exist for these regimes, although the dimensional arguments of Siggia[9] give an exponent $\phi\cong 1$ in agreement with experiment.

The situation should be a lot simpler for fluctuations relaxing above the critical temperature, where sharp interfaces are not stable. The free energy being then bounded, one may drop, in a first approximation, the quartic term in (2.3). Of course, there is no growth of ψ fluctuations now. Rather, their strength can only diminish

$$\frac{d}{dt}\int d^3r\,\psi^2(r,t)=-2\lambda\int d^3r[r_0(\vec{\nabla}\psi)^2+\alpha(\nabla^2\psi)^2]\leq 0\ . \quad (2.4)$$

As we follow only the evolution at scales larger than the correlation length, the α term in the right-hand side of (2.4) is negligible. We have then the typically diffusive result

$$\frac{d}{dt}C_{\text{tot}}=\frac{d}{dt}\int d^3r\,\psi^2(r,t)=-2D_0\int d^3r(\vec{\nabla}\psi)^2\leq 0\ , \quad (2.5)$$

where $D_0=r_0\lambda$.

Still, it is interesting to consider the fate of a distribution of concentration fluctuations centered around some wave number $k_m(0)$ and with a nonvanishing amplitude C_{tot} at a temperature close but above T_c. We will assume that C_{tot} is well above its equilibrium value ($0<<C_{\text{tot}}\leq 1$), and consequently drop the thermal noises that should be retained in (2.1) and (2.2) near equilibrium. Near the consolute temperature T_c the diffusivity D_0 goes to zero (critical slowing down), while the viscosity has only a very weak critical singularity[10,11] and can be taken as a constant in a first approximation. At a temperature a few millidegrees above T_c the

Prandtl number $P=\nu/D_0$ can be as large as 10^6.[13] The quantities of interest to us are the correlation functions

$$U(\vec{k},t)=\frac{1}{2}\int d^3r\, e^{i\vec{k}\cdot\vec{r}}\langle \vec{v}(\vec{r},t)\cdot\vec{v}(0,t)\rangle \tag{2.6a}$$

and

$$S(\vec{k},t)=\frac{1}{2}\int d^3r\, e^{i\vec{k}\cdot\vec{r}}\langle \psi(\vec{r},t)\psi(0,t)\rangle \ . \tag{2.6b}$$

As we discussed in Ref. 14, the α term in (2.1) acts as a dynamical analog of surface tension in that it allows concentration gradients to relax, even at zero diffusivity, by creating fluid flow. This process tends to make the kinetic energy spectrum $U(k,t)$ equal to the gradient energy $2\alpha k^2 S(k,t)$ at each wave number. Due to the nonzero viscosity, however, velocity fluctuations are damped out very fast relative to the concentration, and the equipartition between kinetic and gradient energy is never achieved. The concentration gradients are continously converted into kinetic energy and then dissipated, causing the gradient energy to decrease rapidly,

$$\begin{aligned}\frac{d}{dt}E_g&=\frac{d}{dt}\frac{\alpha}{(2\pi)^2}\int_0^\infty S(k,t)k^4dk\\&=-\frac{2\nu}{(2\pi)^2}\int_0^\infty U(k,t)k^4dk\le 0\ .\end{aligned} \tag{2.7}$$

The decay of the concentration fluctuations is, on the contrary, only proportional to D_0, and can be neglected close to T_c

$$\frac{dC_{\text{tot}}}{dt}=\frac{1}{(2\pi)^2}\int_0^\infty S(k,t)k^2dk=0\ . \tag{2.8}$$

Therefore, if we have a distribution of concentration fluctuations centered around a wave vector $k_m(t)$ at time t, so that

$$C_{\text{tot}}\cong k_m^3 S(k_m)\cong\text{const}\ , \tag{2.9}$$

we find, using (2.7)

$$\begin{aligned}0\le\frac{d}{dt}E_g&\cong\frac{d}{dt}[k_m^5(t)S(k_m(t))]\\&=C_{\text{tot}}\frac{d}{dt}k_m^2(t)\ .\end{aligned} \tag{2.10}$$

Therefore, the characteristic wave number of the fluctuations decreases with time

$$\frac{d}{dt}k_m(t)\le 0\ . \tag{2.11}$$

It is interesting to note that the result (2.11) appears in the work of Kawasaki[15] in the theory of spinodal decomposition. As the above derivation makes clear, however, its validity is not at all limited to temperatures below the critical point.

We have checked (2.11) quantitatively by numerically integrating the equations for $U(k,t)$ and $S(k,t)$ obtained from the quasinormal Markovian closure procedure.[16] These equations take the form

$$\begin{aligned}&(\partial_t+2D_0k^2)S(k,t)=T_s(k,t)\ ,\\&(\partial_t+2\nu k^2)U(k,t)=T_u(k,t)\ ,\end{aligned} \tag{2.12}$$

where the transfer functions $T_{s,u}(k,t)$ are complicated convolution integrals of the U and S spectra over all wave vectors. (See Appendix A). In the limit $D_0=0$, our equations are a generalization for nonequilibrium velocity fluctuations of the mode coupling equations of Ref. 5.

We show in Fig. 2 the result of our calculation for initial conditions like the ones mentioned above, with zero initial velocity, $\alpha=\nu^2$ (Ref. 14) and $P=10^5$. The peak in the concentration spectrum moves towards the small wave numbers while its maximum amplitude grows as $S(k_m(t)))$ $\propto k_m^{-3}(t)$, in agreement with (2.9). The wave number k_m varies as

$$k_m(t)\cong t^{-1/2}\ . \tag{2.13}$$

The behavior shown is independent of the detailed form of the initial spectrum of the fluctuations. In Fig. 3 we plot the scaling function de-

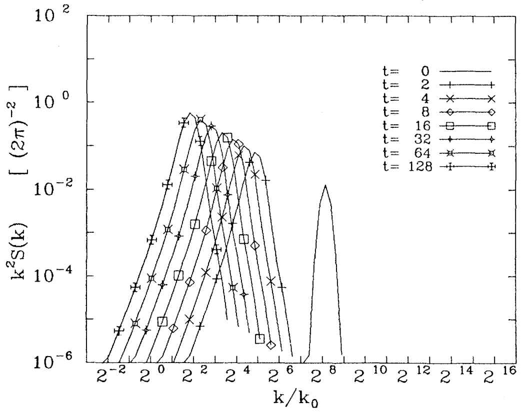

FIG. 2. Time evolution of the concentration spectrum $k^2C(k)$ for $C_{\text{tot}}=1$, $\nu=10^{-2}$, and $P=10^5$. The peaks of the spectrum line up with slope -1. The units of k and t are arbitrary, but consistent with (2.7) and (2.8). Comparison with experiments could be best done by referring the momenta to the inverse correlation length ξ^{-1}, and the times to $D\xi^{-2}$, while holding the ratio K of (2.17) constant. K was equal to 10^{-3} in our calculation.

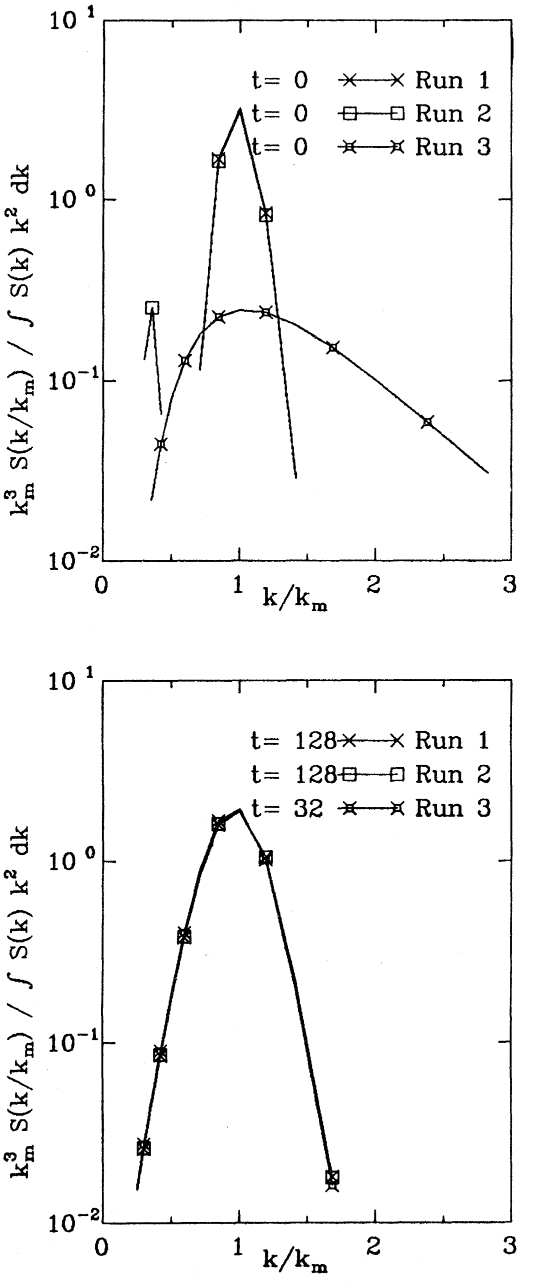

FIG. 3. Evolution towards the scaling function F for different numerical runs. The runs had all the same values of C_{tot}, α, ν, and D of Fig. 1 (run 1). The time and momentum units are also in Fig. 1. Run 2 was exactly as run 1 but with a triply-peaked initial spectrum. The spike at the smallest k in *a* corresponds to one of these satellite peaks. The other, that was symmetrical with respect to the central one, does not show in this plot. Run 3 had a differently shaped initial distribution.

fined in (1.3) for three typical runs, both at the same temperature and with the same value of C_{tot} but with a different $S(k,t=0)$. We see that after an initial transient time, F takes a form independent of time and of the initial conditions. Those of run 2, in particular, had a three-peaked initial spectrum $S(k,t=0)$, with the central peak coinciding with that of run 1. We observe that the memory of the satellite peaks is rapidly lost. Both the shape and the numerical values of the scaling function F that we obtain are very similar to those of Ref. 7. We discuss the possible relevance of this fact in the next section.

The scaling results (1.3) and (2.13) and the universality of the scaling function F can be proven from our closure equations to be exact in the limit $D_0=0$. (See Appendix B.) Alternatively, one can perform in (2.12) a partial integration over wave vectors larger than $k_m(t)$, and obtain and approximate equation of motion for $S(k,t)$ with $k<k_m(t)$ of the form (see Appendix A)

$$(\partial_t+2D_0k^2)S(k,t)=2Dk^2S(k,t)\ , \tag{2.14}$$

where

$$D=\frac{4\alpha}{3\pi^2\nu}C_{\text{tot}}\ . \tag{2.15}$$

According to (2.14), large scale concentration fluctuations at $k<k_m$ grow, if $D>D_0$, with the characteristic frequency Dk^2. This is the same frequency at which the concentration gradients are converted into velocity fluctuations by the α term.[17] We can now get (2.13) from (2.14) and (2.15) by adapting an argument due to Binder and Stauffer.[8] The growth of a fluctuation of diameter k_m^{-1} should obey, on dimensional grounds,

$$\frac{dk_m(t)}{dt}=Dk_m^3(t)=\frac{4\alpha}{3\nu}C_{\text{tot}}k_m^3(t)\ , \tag{2.16}$$

which yields (2.13) if D_0 is small enough for (2.9) to hold.

Although our results are strictly valid only in the limit $D_0=0$, Eq. (2.14) and our numerical results suggest that they will not change much for a nonzero diffusivity provided that the ratio

$$K=\frac{D_0}{D} \tag{2.17}$$

is much smaller than one. In this limit, we obtain from (2.5), (2.9), and (2.13) an extremely slow decay of the concentration fluctuations

$$C_{\text{tot}}(t)\cong C_{\text{tot}}(0)t^{-K}\ . \tag{2.18}$$

If the values of the temperature and C_{tot} are such that $K \lesssim 1$, the fluctuations will still migrate towards the large scales, but our scaling results will not hold. Finally, if we are away from the critical point or the fluctuations are very weak, so that $K << 1$, we expect them to decay diffusively in the usual manner.

It is also interesting to note that because the migration frequency Dk^2 and the diffusive frequency D_0k^2 both scale (if $D >> D_0$ so that C_{tot} is constant) as the same power of the wave number, the migration of the concentration fluctuations will only stop when they reach the boundaries of the system. They will then pile up at the minimum wave number $k_{\min}$ and relax extremely slowly towards their equilibrium level in a characteristic time $(D_0k_{\min}^2)^{-1}$ which can be of the order of days. One can accept this shockingly long life time of a nonequilibrium fluctuation by realizing that the system gets, in some sense that we explain below, into a state of negative temperature. To understand this, it is useful to consider the long time behavior of the fluctuations in the limit $D_0=0$. If the diffusion constant vanishes, a steady state is eventually reached. To find it, we follow Ref. 18 and define the entropy functional

$$\Omega(t)=\tfrac{1}{2}\int\frac{d^3k}{(2\pi)^3}[2\ln U(k,t)+\ln S(k,t)] \ . \tag{2.19}$$

In Appendix C we prove from the closure equation (2.12) that $\Omega(t)$ is monotonically increasing,

$$\frac{d}{dt}\Omega(t)\geq 0 \ . \tag{2.20}$$

The steady state of constant $\Omega(t)$ is obtained when

$$S(p)=\frac{1}{B+\alpha p^2} \ , \tag{2.21}$$

where the susceptibility B takes the value necessary to make (2.21) consistent with (2.9). It is easy to see that large enough values of $k_{\min}^2C_{\text{tot}}$ will require B to be negative. The system is then locked into a metastable state of negative susceptibility. For a small but nonvanishing D_0 this state will persist with a time dependent B that adiabatically adjusts itself to the (slowly) changing C_{tot}. Eventually, of course, at times longer than $(D_0k_{\min}^2)^{-1}$, $B(t)\rightarrow r_0$. It should be added here that the metastable state just described has mainly a conceptual interest, and its experimental detection might be very difficult.

III. CONCLUSIONS

The main results (2.13) and (1.3) of the previous section suggest that a process similar to spinodal decomposition might be observed in liquid binary mixtures above the critical consolute temperature T_c. Wong and Knobler[19] have reported the results of a "double quench" experiment in an isobutyric acid and water mixture, in which after they brought their system into the two-phase region and let it coarsen for some time, the quench was reversed and the scattering experiment was continued as the mixture tried to reach the one-phase equilibrium. Their data are in qualitative agreement with our conclusions, with the maximum of the structure factor moving towards small wave vectors and a very slowly decaying C_{tot} although they are not complete enough to permit a quantitative comparison with our theory.

There are two ways we can imagine in which one could experimentally verify the results of this paper. One, of course, is to improve the results of the experiment of Ref. 19. In such an experiment the three variable parameters are the temperatures T_1 and T_2, above and below T_c, respectively, that limit the quenches, and the length of time Δt that the mixture is allowed to stay in the two-phase region. Our results should hold independently of the values of these three parameters provided that they result in a K much smaller than 1 in (2.17). Because the time variation of C_{tot} in the spinodal region is not well established theoretically, we cannot give a more explicit criterion.

The efficiency of the double quench experiments is limited by the small width $\Delta\psi$ of the miscibility gap at the small quench depths at which the experiments must be performed. Because a smaller value of $\Delta\psi$ means smaller value of C_{tot},[3] it may be difficult to attain small enough values of K for the scaling results (2.13) and (1.3) to hold. Much bigger values of C_{tot} can be obtained if the results of Ref. 16 hold. There we showed that at temperatures close to T_c violent stirring of a binary liquid which was initially unmixed results in the formation of a long-lived metastable state of partial mixing in which the concentration fluctuations are pinned at a wave number k_* proportional to the Reynolds number of the turbulence. k_* is such that the tendency towards complete mixing provided by the turbulence is just balanced by the desire of the fluctuations to go to small wave numbers as we have discussed above. If the stirring force keeping the mixture in the turbulent state is turned off before this metastable state decays, the migration of the concentration fluctuations towards the large scales could be observed. A detailed theory of such an experiment, however, should take into account the temporal decay of the turbulence and is beyond the scope of this paper.

Finally, we like to comment on the relevance of this work to the theory of spinodal decomposition in fluids. In principle, nothing in our argumentation restricts the validity of (2.13) and (1.3) to regimes above the critical temperature. Indeed, after the initial period during which Binder's $k_m(t) \cong t^{-1/3}$ holds and C_{tot} grows with time, the experimental data of Ref. 7 suggest that C_{tot} stays constant and the scaling function F is the same we calculated in Fig. 3. Although Chou and Goldburg did not try to fit their data to our result (2.13), it seems to us that $\phi \cong \frac{1}{2}$ could be consistent with their experimental results in a limited time interval sandwiched between the regimes with $\phi \cong \frac{1}{3}$ and $\phi \cong 1$, and the migration mechanism that we have described in section be responsible for the departure of the experimental data and the Kawasaki-Otha results from the $\phi = \frac{1}{3}$ behavior. In addition, using the estimates of Ref. 9 for the $\phi \cong 1$ regime together with our (2.13) for $\phi = \frac{1}{2}$ gives a reasonable value for the time at which the crossover between both regimes takes place. However, it is very difficult to accurately fit so many power law exponents to data which span relatively narrow ranges. This is why the study of experimental conditions where sharp interfaces are not stable should be more suitable for the testing of our results.

ACKNOWLEDGMENTS

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APPENDIX A: CLOSURE EQUATIONS

To derive a closed system of equations for the spectra (2.6) we assume initial conditions with Gaussian statistics (quasinormal approximation) and that the velocity and concentration fluctuations are initially decoupled. This results in equations for $U(k,t)$ and $S(k,t)$ at time t that contain integrals over the past values $U(k,s)$ and $S(k,s)$ of the spectra at all the earlier times s. One then Markovianizes these equations by updating the spectra to time t. (See Refs. 14 and 20 for details of the algebra.) The result is

$$[\partial_t + 2\lambda_0 k^2(r_0+\alpha k^2)]S(k,t) = \frac{k}{(2\pi)^2}\int_{\Delta_k}\int dp\,dq \left[\frac{\sin\beta}{k}\right]^2 \theta^{(1)}_{kpq}pq^3 \times\{\,U(p)[S(q)-S(k)] - 2\alpha(k^2-q^2)S(k)S(q)\,\} \tag{A1}$$

and

$$(\partial_t + 2\nu k^2)U(k,t) = \frac{1}{(2\pi)^2 k}\int_{\Delta_k}\int dp\,dq \left[\frac{\sin\beta}{k}\right]^2 \theta^{2}_{kpq}p^3q^3(p^2-q^2) \times[\alpha^2(p^2-q^2)S(p)S(q) - \alpha S(q)U(k)]\ , \tag{A2}$$

where the momenta (k,p,q) are required to form a triangle of which β is the angle opposite to wave vector k. The relaxation times $\theta^{(i)}_{kpq}$ are[14]

$$\theta^{(i)}_{kpq} = \frac{1-e^{-\mu^{(i)}_{kpq}t}}{\mu^{(i)}_{kpq}} \quad (i=1,2) \tag{A3}$$

with

$$\mu^{(1)}_{kpq} = D(k^2+q^2)+\nu p^2\ ,$$
$$\mu^{(2)}_{kpq} = D(p^2+q^2)+\nu k^2\ . \tag{A4}$$

Our equations are exact in the limit $t \to 0$, and coincide, if $D_0=0$, with those of Ref. 5 if the velocity fluctuations are in equilibrium [$U(k)$ = constant]. We will find that if C_{tot} is not small $U(k)$ departs from its equilibrium value (see Fig. 4), and therefore keep Eq. (A2) in our description.

To derive (2.14) we expand the transfer integral in (A1) in the limit of $\lambda_0=0$ and $p,q \cong k_m >> k$ and find, in lowest order,

$$\partial_t S(k,t) = -\frac{1}{3\pi^2 \nu} k^2 S(k,t) \times \int_k^\infty dq [U(q,t)+2\alpha(k^2-q^2)S(q,t)] + \frac{1}{3\pi^2}\frac{k^2}{\nu}\int_k^\infty dq\, U(q)S(q) . \tag{A5}$$

This result is a familiar one close to equilibrium, although it is usually derived very differently. Substituting in it the equilibrium spectra

$$U(q)=2 , \quad S(q)=\frac{1}{B+\alpha A q^2} , \quad B=r_0 , \tag{A6}$$

results , in the limit $k \to 0$, in

$$[\partial_t + 2\lambda_R k^2(r_0+\alpha k^2)]S(k,t) = 2\lambda_R k^2 , \tag{A7}$$

where we have defined the renormalized transport coefficient

$$\lambda_R = \frac{1}{6\pi\nu\sqrt{r_0\alpha}} . \tag{A8}$$

Observe that the same transport coefficient appears in the dissipative part of (A7) and in the amplitude of the thermal forcing. This is just a consequence of the familiar fluctuation-dissipation theorem.[21] Restoring physical units (A8) is the well-known Kawasaki-Stokes relation.[10]

We are interested in situations at nonzero wave vector and with fluctuations that are well above the thermal equilibrium level (A6). Nevertheless, the interpretation of (A7) as providing a nonequilibrium renormalized transport coefficient should still make sense.[22] Because $\nu >> D$ we can neglect $U(q)$ in (A7), and because we are considering only concentration modes at scales larger than the correlation length, the dissipative term proportional to k^4 can also be dropped. We then obtain (2.14).

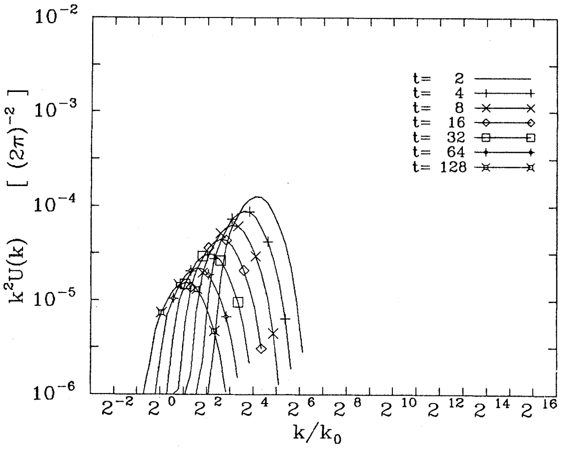

FIG. 4. Evolution of the kinetic spectrum $k^2U(k)$ for the conditions of Fig. 1. At $t=0$, $U(k)=0$. The peaks in the spectrum line up with a + 1 slope, a manifestation of the tendency towards equipartition of kinetic and gradient energy brought by the α coupling.

APPENDIX B: DERIVATION OF THE SCALING RESULTS

We look for self-similar solutions of the form

$$S(k,t)=t^{\alpha}F(kt^{\beta}) , \quad U(k,t)=t^{\alpha-2\beta}k^2G(kt^{\beta}) , \tag{B1}$$

to the closure Eqs. (A1) and (A2). In the limit $\lambda_0=0$ (2.9) imposes the restriction

$$\alpha=3\beta . \tag{B2}$$

Substitution of (B2) and (B1) in (A1) and (A2) yields the relations

$$\left[\alpha+\beta k'\frac{d}{dk'}\right]F(k')=t^{1-2\beta}T_s'(k') , \quad \left[\alpha+\beta k'\frac{d}{dk'}\right]G(k')=t^{1-2\beta}T_u'(k') + 2\nu k'^2 t^{1-2\beta}G(k') , \tag{B3}$$

where $k'=kt^{\beta}$ and $T_{u,s}'$ are obtained from (A1) and (A2) by replacing $S(k,t)$ by $F(k')$ and $U(k,t)$ by $k'^2 2G(k')$. As seen from (B3), scaling holds if

$$\beta=\tfrac{1}{2} , \quad \alpha=\tfrac{3}{2} \tag{B4}$$

in agreement with (2.9) and (2.13).

APPENDIX C: DERIVATION OF (2.20)

We start by writing (A1) and (A2) in the more symmetrical, but equivalent, form

$$\partial_t S(k,t) = \int\int \frac{d^3p}{(2\pi)^3}\frac{d^3q}{(2\pi)^3}\delta^{(3)}(\vec{k}+\vec{p}+\vec{q})\left[\frac{\sin\beta}{k}\right]^2 \theta_{kpq}k^2p^2\{ U(p)[S(q)-S(k)]-2\alpha(k^2-q^2)S(k)S(q) \} , \tag{C1}$$

$$(\partial_t+\nu k^2)U(k,t)=\int\int\frac{d^3p}{(2\pi)^3}\frac{d^3p}{(2\pi)^3}\delta^{(3)}(\vec{k}+\vec{p}+\vec{q})\left[\frac{\sin\beta}{k}\right]^2\theta_{kpq}q^2p^2(p^2-q^2)$$

$$\times[\alpha^2(p^2-q^2)S(p)S(q)-\alpha S(q)U(k)]+\tfrac{1}{2}\langle\,|\vec{f}_v(k)|^2\rangle\;, \tag{C2}$$

where we have taken the limit $\lambda_0=0$ and included the thermal forcing in the velocity equation to insure a proper relaxation to equilibrium. Using the definition (2.19) of the entropy Ω, we find, after considerable algebra,

$$\frac{d}{dt}\Omega=\int\frac{d^3k}{(2\pi)^3}\frac{d^3p}{(2\pi)^3}\frac{d^3q}{(2\pi)^3}\delta^3(\vec{k}+\vec{p}+\vec{q})\left[\frac{\sin\beta}{k}\right]^2\frac{p^2q^2}{\nu k^2}U(k)S(p)S(q)\left[\frac{\alpha(p^2-q^2)}{U(k)}-\frac{1}{2}\left[\frac{1}{S(p)}-\frac{1}{S(q)}\right]\right]^2$$

$$-\int\frac{d^3k}{(2\pi)^3}\left[\nu k^2-\frac{\langle\,|\vec{f}_v(k)|^2\rangle}{2U(k)}\right]. \tag{C3}$$

In a first stage, after the position of the maximum of the structure factor reaches the minimum avalaible wave vector $k_{\min}$, the velocity fluctuations will decay relatively rapidly to the thermal distribution (A6) in a time of the order $(\nu k_{\min}^2)^{-1}$ or so, and therefore the second integral in (C8) will vanish. We then have the result

$$\frac{d}{dt}\Omega\geq 0 \tag{C4}$$

which we set to prove.

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[1] See, for instance, the articles by W. I. Goldburg and J. S. Huang and by J. Langer in *Fluctuations, Instabilities, and Phase Transitions,* edited by T. Riste (Plenum, New York, 1975).

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[22] The technique of expanding the transfer integrals around very elongated triads is familiar in the context of turbulent theory. It can be used, for instance, to obtain turbulent renormalization of transport coefficients, like Richardson's law. See, for instance, Refs. 14 and 17 and references therein.