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Critical slowing of chemical reactions

Scott T. Milner and Paul C. Martin
Department of Physics and Division of Applied Sciences, Harvard University, Cambridge, Massachusetts 02138

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Procaccia and Gitterman have suggested that the reaction rates of chemically reacting binary mixtures are drastically reduced near their thermodynamic critical points and that this reduction is responsible for anomalies observed in a series of experiments performed more than 15 years ago. A more detailed analysis shows that this suggestion is untenable, that spatially uniform composition fluctuations are not drastically retarded at thermodynamic critical points, and that spatially varying composition fluctuations are at best slowed down over a small range of wavenumbers that will be difficult to detect experimentally. A qualitative picture is provided by mean-field and Van Hove theory. Quantitative corrections are obtained with use of renormalization-group techniques. At small and large wavenumbers, the hydrodynamic modes most affected near the critical point are, respectively, thermal and particle diffusion. The mode-couplings relevant in these regimes differ from the mode couplings relevant at intermediate wavelengths where the critical slowing of a reaction might be observable.

I. INTRODUCTION

Interest in the properties of chemically reacting systems near liquid-gas or consolute critical points was rekindled in 1981 when Procaccia and Gitterman[1] (PG) asserted that the rates of chemical reactions might be drastically reduced near second-order liquid-gas or phase-separation critical points. They argued that this reduction would be especially large in binary chemical mixtures, and suggested that it explained the anomalies observed in a series of experiments performed by Krichevskii and co-workers.[2]

In this paper, we present simple physical arguments that modify this conclusion and restrict its domain of relevance. Using the "Van Hove"[3] or conventional theory of critical slowing down, we show that at long wavelengths, the chemical reaction rate is only weakly suppressed, at most as $(T-T_c)^\alpha$, where α is the specific heat critical exponent, as the temperature T approaches the critical temperature T_c. It is the thermal diffusion mode that is suppressed strongly as the wavenumber $k \rightarrow 0$ and $T \rightarrow T_c$.

This conclusion follows directly from the conservation laws. However slow the chemical process may be, at sufficiently long wavelengths its fixed reaction rate must exceed the thermal relaxation rate—a rate that must vanish with increasing wavelength since energy is conserved. As a result, in an "infinite" system, at long enough distances and times, the "microscopic" chemical and "fast" sound-wave processes reach local equilibrium before the energy. At longer times and distances, the appropriate specific heat, or entropy density susceptibility, is $(\partial s/\partial T)_{\mu,p}$. This specific heat diverges strongly at the critical point and leads to the well-known slowing of heat transport. On the shorter time scale appropriate to the chemical reaction, the entropy and mass density are time-independent. Thus, the susceptibility appropriate to the "chemical concentration variable" is $(\partial c/\partial \mu)_{s,\rho}$ which does not diverge. [When the reaction time is longer than the time required for sound waves or boundary effects to equalize pressures, this susceptibility is replaced by the weakly diverging $(\partial c/\partial \mu)_{s,p}$.]

The situation is different at constant pressure at wavelengths shorter than a "crossover" wavelength, a wavelength at which heat diffusion and chemical relaxation take the same time. A "Van Hove analysis" identifies this wavelength and predicts, in accord with physical arguments, that at shorter wavelengths, the slowest mode—which may in some sense be identified as a "chemical relaxation" mode—relaxes isobarically and isothermally and is therefore strongly suppressed near the critical point.

As in other systems, long-lived fluctuations and nonlinearities modify the Van Hove analysis of the dynamics and the dispersion relations of the hydrodynamic modes of chemically reacting systems near their critical points. To calculate the dynamic exponents, which differ in different wavelength regimes, we use the renormalization group (RG). At the longest wavelengths, the coupling of the slow heat mode to the velocity is relevant and the dynamical modes of the system reduce to those of Model H of Halperin, Hohenberg, and Siggia.[4] At intermediate wavelengths, where the slow mode is most closely related to the chemical reaction rate, its coupling to a fast heat-like mode leads to the behavior described by Model C of Halperin and Hohenberg.[5] This is the regime to which the RG discussion of PG applies. Although their discussion concludes correctly that velocity couplings are irrelevant, it incorrectly omits this relevant conserved-energy-coupling. At shorter wavelengths, where the chemical diffusion rate exceeds the chemical reaction rate and it is permissible to treat the concentration as if it were conserved, the system is once again described correctly by Model H.

II. VAN HOVE THEORY

In the conventional theory of critical slowing down, the dynamical extension of mean-field theory, the "hydrodynamic" equations of motion for the thermodynamic "fields" $\boldsymbol{\psi}$ (e.g., the density, concentration, and entropy density) and their conjugate "potentials," $\boldsymbol{\phi}$ (e.g., the pressure, chemical potential, and temperature) take the form

$$-i\omega\boldsymbol{\psi}(k,\omega) = \Gamma(k)\boldsymbol{\phi}(k,\omega) = \Gamma(k)\chi^{-1}(k,t)\boldsymbol{\psi}$$

or (2.1)

$$-i\omega\boldsymbol{\psi}(k,\omega) \equiv M\boldsymbol{\psi} \, .$$

In these equations, Γ is the matrix of Onsager coefficients, and χ^{-1} is the inverse of the susceptibility matrix as a function of reduced temperature t. The combination $M \equiv \Gamma\chi^{-1}$, is called the hydrodynamic matrix. The relaxation processes described by Γ are assumed to be short-ranged and local—and therefore unaffected by long-wavelength critical fluctuations. In this approximation, which should be rigorous in more than four dimensions, the singular dependence of the hydrodynamic mode frequencies results entirely from the fact that two eigenvalues of χ^{-1} vanish as t^{γ} and t^{α}.

If, for convenience, we choose new variables $\boldsymbol{\psi}' = \Lambda\boldsymbol{\psi}$ to make χ^{-1} diagonal, and assume that χ^{-1} has one entry that vanishes as t^{γ} (where γ is the susceptibility exponent), it is easy to see that the smallest eigenvalue of M is suppressed to zero as $t \to 0$. Clearly, *some* eigenvalue of M goes to zero, because det $M \to 0$. Moreover, as we recall from degenerate quantum mechanical perturbation theory, a perturbation between two nearly degenerate levels that cross as a function of a parameter leads to a "repulsion" that eliminates the crossing. In this mathematically similar problem, it is the smallest eigenvalue of M (at each value of the wavenumber) that is suppressed as $t \to 0$.

The binary system[6] discussed in PG contains six hydrodynamic degrees of freedom—the chemical concentration difference, c, the entropy density, s, the mass density, ρ, and the velocity, $\mathbf{v}$. Since the transverse components of the velocity are uncoupled, the 6×6 matrix that describes the linear hydrodynamics of the system can be immediately reduced to a 4×4 matrix. When the ordinary sound mode, to which the density and longitudinal velocity give rise, is much faster than the nonpropagating (diffusive and reacting) modes, they can also be eliminated, leaving a pair of equations—the conservation law for s,

$$\rho T\frac{\partial s}{\partial t} = -\nabla\cdot q \, , \tag{2.2}$$

and the equation for c in which the conservation law for the mass of each species is violated by the chemical reaction

$$\rho\frac{\partial c}{\partial t} = -\nabla\cdot i + \rho r A \, . \tag{2.3}$$

In Eqs. (2.2) and (2.3), q and i are entropy and concentration currents, A (or $-\mu$) is the affinity, and r is related to the speed of the chemical reaction.

Expanding the currents with the aid of the constitutive relations and the Onsager relations, we obtain[7]

$$\frac{\partial}{\partial t}\begin{bmatrix} s \\ c \end{bmatrix} = -\begin{bmatrix} \dfrac{\gamma}{\rho T}k^2 & \dfrac{\beta}{\rho}k^2 \\ \dfrac{\beta}{\rho}k^2 & r+\dfrac{\alpha}{\rho}k^2 \end{bmatrix}\begin{bmatrix} \delta T \\ \delta\mu \end{bmatrix} = \Gamma\begin{bmatrix} \delta T \\ \delta\mu \end{bmatrix} , \tag{2.4}$$

$$\begin{bmatrix} \delta T \\ \delta\mu \end{bmatrix} \approx \chi^{-1}\begin{bmatrix} \delta s \\ \delta c \end{bmatrix} = \begin{bmatrix} \left(\dfrac{\partial T}{\partial s}\right)_c & \left(\dfrac{\partial T}{\partial c}\right)_s \\ \left(\dfrac{\partial \mu}{\partial s}\right)_c & \left(\dfrac{\partial \mu}{\partial c}\right)_s \end{bmatrix}\begin{bmatrix} \delta s \\ \delta c \end{bmatrix} , \tag{2.5}$$

where the deviation of each thermodynamic variable, x, from its equilibrium value is denoted by δx, and where $A_{eq} = -\mu_{eq} = 0$.

III. STATIC SUSCEPTIBILITIES

Having identified δs and δc as the important degrees of freedom, and the derivatives at constant pressure in Eq. (2.5) as the appropriate susceptibilities, we can make contact with the rules of Griffiths and Wheeler[8] (GW). These rules relate the divergences of thermodynamic derivatives to the orientation and position of the coexistence surface (CXS) and critical line (CRS) in "thermodynamic potential" (T,p,μ) space.

Suppose that the CXS is not exceptionally oriented. Then, the rules of GW require that all elements of χ^{-1} vanish "weakly" as the CRS is approached, while $(\partial T/\partial s)_{\mu}$, etc., vanish "strongly." In other words, in a notation suggestive of the ferromagnet, with distance from the CXS denoted by h, and distance along the CXS from the CRS denoted by t, the quantity $(\partial T/\partial s)_c$ behaves as t^{α} for $h=0$, and as $h^{\alpha/\beta\delta}$ for $t=0$, while $(\partial T/\partial s)_{\mu}$ behaves as t^{γ} for $h=0$, and as $h^{(\delta-1)/\delta}$ for $t=0$.

The determinant

$$\det\chi^{-1} = \frac{\partial(T,\mu)}{\partial(s,c)} = \left(\frac{\partial T}{\partial s}\right)_{\mu}\left(\frac{\partial \mu}{\partial c}\right)_s = \left(\frac{\partial T}{\partial s}\right)_c\left(\frac{\partial \mu}{\partial c}\right)_T \tag{3.1}$$

vanishes "strongly" times "weakly." Two simple changes of variables diagonalize χ^{-1} and display these thermodynamic divergences manifestly. If we let

$$\delta s_r = \delta s - \left(\frac{\partial s}{\partial c}\right)_T \delta c \equiv \delta s - \eta\delta c$$

and

$$\delta c_r = \delta c - \left(\frac{\partial c}{\partial s}\right)_T \delta s \equiv \delta c - \bar{\eta}\delta s \, , \tag{3.2}$$

we obtain

$$\chi^{-1}_{s_r,c} = \begin{bmatrix} \left[\dfrac{\partial T}{\partial s}\right]_c & 0 \\ 0 & \left[\dfrac{\partial \mu}{\partial c}\right]_T \end{bmatrix}$$

and

$$\chi^{-1}_{s,c_r} = \begin{bmatrix} \left[\dfrac{\partial T}{\partial s}\right]_\mu & 0 \\ 0 & \left[\dfrac{\partial \mu}{\partial c}\right]_s \end{bmatrix} . \tag{3.3}$$

Aside from exceptional cases, η and $\bar{\eta}$ are finite on the CRS; in fact, $\eta\bar{\eta} \rightarrow 1$. The two changes of variable are regular at the critical point.

From either diagonal form of χ^{-1}, we can construct a field theory of the thermostatics and fluctuations with the exponents anticipated by GW. In mean field theory (MFT), we have

$$\left[\frac{\partial T}{\partial s}\right]_c (k,t) \approx \left[\frac{\partial T}{\partial s}\right]_c (k=0,t=1)$$

and

$$\left[\frac{\partial \mu}{\partial c}\right]_T (k,t) \approx \left[\frac{\partial \mu}{\partial c}\right]_T (k=0,t=1) \left[t + \frac{k^2}{\Lambda^2}\right] \tag{3.4}$$

where Λ is some microscopic cutoff. If we introduce the scaled variables

$$q_r \equiv s_r \left[\frac{\partial T}{\partial s}\right]_c^{1/2} (k=0,t=1)$$

and

$$\psi \equiv \frac{c}{\Lambda^{1/2}} \left[\frac{\partial \mu}{\partial c}\right]_T^{1/2} (k=0,t=1) , \tag{3.5}$$

we can write a free energy that includes all the relevant couplings

$$-\beta F = \int d^d x \mathcal{F} ,$$

$$\mathcal{F} \equiv \frac{(\nabla\psi)^2}{2} + \kappa^2 \frac{\psi^2}{2} + \frac{q_r^2}{2} + \gamma q_r \frac{\psi^2}{2} + u\frac{\psi^4}{4!} . \tag{3.6}$$

In MFT, the inverse square coherence length ξ^{-2} is given by $\kappa^2 = t\Lambda^2$. This expression agrees with the GW picture with the following identifications:

$\langle cc \rangle = \chi_c \approx n=1$ ferromagnetic susceptibility ,

$\langle s_r s_r \rangle = \chi_{s_r} \approx$ specific heat ,

and

$$\langle ss \rangle = \langle (s_r + \eta c)(s_r + \eta c) \rangle = \langle s_r s_r \rangle + \eta^2 \langle cc \rangle .$$

Two "exceptional cases" are worth noting. Consider first a single-component system undergoing an ordinary-liquid-gas transition, but with molecules "colored" red or blue. The "coloring" is pedantic and does not affect the microscopic Hamiltonian in any way. Hence the coexistence surface and critical line in (T,p,μ) space are just the coexistence line and critical point in (T,p) space translated parallel to the μ-axis and $\bar{\eta}=0$. Consequently χ^{-1} is already diagonal, both $(\partial T/\partial s)_\mu$ and $(\partial T/\partial s)_c$ vanish strongly, and both $(\partial\mu/\partial c)_s$ and $(\partial\mu/\partial c)_T$ are finite at the critical line. The concentration variable, c, is irrelevant.

It is more difficult to find a symmetry that even "pedantically" leads to the other exceptional case (mentioned by PG) where s is "irrelevant" at a phase-separation transition for which c is the order parameter. If there were such a system, with $\eta=0$, its specific heat, $\partial s/\partial T$, would be finite, while $\partial c/\partial\mu$ would diverge strongly. Its CRS would be parallel to the T-axis.

IV. MODE FREQUENCIES

In this section we calculate the two mode frequencies, accessible to scattering experiments. In the Van Hove approximation, the calculation reduces to a simple eigenvalue problem

$$\det (M - i\omega I) = 0 . \tag{4.1}$$

If we set $r \equiv i\omega$, we expect to obtain two positive real roots, $r_>$ and $r_<$, to the equation

$$0 = r^2 - r \operatorname{tr} M + \det M , \tag{4.2}$$

with

$$\begin{aligned} \det M = r_> r_< &= \det \Gamma \det \chi^{-1} \\ &= \left[\frac{\gamma}{\rho T} k^2 \left[r + \frac{\alpha}{\rho} k^2 \right] - \left[\frac{\beta}{\rho} k^2 \right]^2 \right] \left[\frac{\partial T}{\partial s}\right]_\mu \left[\frac{\partial \mu}{\partial c}\right]_s \end{aligned} \tag{4.3}$$

and

$$\begin{aligned} \operatorname{tr} M &= r_> + r_< \\ &= \frac{\gamma}{\rho T} k^2 \left[\frac{\partial T}{\partial s}\right]_c + \left[r + \frac{\alpha}{\rho} k^2 \right] \left[\frac{\partial \mu}{\partial c}\right]_s \\ &\quad + \frac{\beta}{\rho} k^2 \left[\left[\frac{\partial T}{\partial c}\right]_s + \left[\frac{\partial \mu}{\partial s}\right]_c \right] . \end{aligned} \tag{4.4}$$

We note that det M vanishes "strongly" times "weakly," (i.e., as $t^{\gamma+\alpha}$) while tr M vanishes "weakly" (i.e., as t^α). We can therefore make the approximations

$$\begin{aligned} r_> &= \operatorname{tr} M - r_< = \operatorname{tr} M + O(t^\gamma) , \\ r_< &= \frac{\det M}{r_>} = \frac{\det M}{\operatorname{tr} M} + O(t^{2\gamma-\alpha}). \end{aligned} \tag{4.5}$$

The roots, which are not simple power laws, define several length scales independent of t and k:

(1) The first of these scales is related to k_C, defined by

$$r \equiv \left[\frac{\alpha}{\rho} - \frac{T\beta^2}{\rho\gamma}\right] k_C^2 \,, \tag{4.6}$$

or $r(\partial\mu/\partial c)_s \approx (\alpha/\rho)(\partial\mu/\partial c)_s k_C^2$. Since the equations

$$r\left[\frac{\partial\mu}{\partial c}\right]_s \equiv \frac{1}{\tau} \tag{4.7}$$

and

$$\frac{\alpha}{\rho}\left[\frac{\partial\mu}{\partial c}\right]_s \equiv D \tag{4.8}$$

describe a chemical relaxation time and chemical diffusion coefficient, k_C^{-1} identifies the length scale at which local chemical relaxation and chemical diffusion are equally effective. For $k \ll k_C$, local relaxation of δc by chemical processes is faster than relaxation by diffusion; for $k \gg k_C$, diffusion dominates chemical relaxation. Of course, since we expanded $\Gamma(k)$ about $k=0$, we can only use this estimate when it yields a value for k_C that is small compared to the microscopic length scale involved in the expansion of $\Gamma(k)$; if the definition yields a "microscopic" value for k_C in some system (because the chemical reaction is strong or particle diffusion is slow), particle diffusion will not be seen in that system.

(2) A second length scale is related to k_H, which is defined by

$$\left[\frac{\gamma}{\rho T} - 2\eta\frac{\beta}{\rho} + \eta\bar{\eta}\frac{\alpha}{\rho}\right]\left[\frac{\partial T}{\partial s}\right]_c k_H^2 \equiv r\left[\frac{\partial\mu}{\partial c}\right]_s \,. \tag{4.9}$$

Ordinarily, heat diffuses more rapidly than particles, i.e., both $\eta\beta/\rho$ and $\eta\bar{\eta}\alpha/\rho$ are smaller than $\gamma/\rho T$. Thus, the length k_H^{-1}, which is related to the thermal diffusion coefficient,

$$\frac{\gamma}{\rho T}\left[\frac{\partial T}{\partial s}\right]_c \equiv D_T \,, \tag{4.10}$$

by

$$D_T k_H^2 \equiv \frac{1}{\tau} \,, \tag{4.11}$$

is generally larger than k_C^{-1}. (If it were not, the slowest mode would be associated with heat transport *at all wavenumbers* , and there would be no mode crossover.) When $k \ll k_H$, the chemical reaction is more rapid than both heat conduction and particle diffusion.

The absolute sizes of k_H and k_C can be altered by varying the chemical properties of the system, i.e., by varying τ. As noted above, the "wavenumber window," in which the relaxation is dominated by chemistry and slower than thermal relaxation is bounded below by k_C and above by k_H. It is therefore natural to introduce the parameter, f, defined as

$$\frac{k_C^2}{k_H^2} = \frac{D_T}{D} \equiv f \,.$$

For dense liquids, in which particle diffusion is impeded while heat diffusion is not, f can have a value of 100 or more. For a reaction rate of 0.1 MHz, a thermal diffusivity of 0.1 cm^2/sec, and a particle diffusivity of 10^{-5} cm^2/sec, we have $f = 10^4$, $k_H = 10^{-3}\ \text{cm}^{-1}$, and $k_C = 10^{-5}\ \text{cm}^{-1}$. Even under these conditions, the "window" only includes two wavenumber decades.

(3) A third length scale is related to k_P, defined by $k_P^{-1} = c\tau$ (where c is the velocity of sound and τ the relaxation time away from the critical point). The 2×2 matrix analysis above was restricted to $k \gg k_P$. For $k \ll k_P$, the argument in the introduction applies and the reaction rate, $r(\partial\mu/\partial c)_{s,p}$, is unaffected by the phase transition.

For a sound velocity $c \approx 1000$ m/sec and $\tau^{-1} \approx 0.1$ MHz, we have $k_P \approx 1\ \text{cm}^{-1}$. As in the case of k_C, we should recall that hydrodynamics applies only when the mean free path, L_{mfp}, satisfies $L_{\text{mfp}} \ll L_P = k_P^{-1}$. Thus for $L_{\text{mfp}} \approx 10^{-7}$ cm and $c \approx 1000$ m/sec, "nonlocal" hydrodynamic phenomena have no effect on the local energy and particle density for reactions with time constants shorter than a picosecond.

In terms of these diffusion and time constants, Eqs. (4.3) and (4.4) take the form

$$\operatorname{tr} M \approx \frac{1}{\tau} + D_T k^2 \,, \tag{4.3$'$}$$

$$\det M \approx \left[\frac{1}{\tau} + Dk^2\right]\left[\frac{\partial T}{\partial s}\right]_\mu \frac{\gamma}{\rho T} k^2 \,, \tag{4.4$'$}$$

whence Eq. (4.5) becomes

$$r_> \approx \frac{1}{\tau} + D_T k^2 = \left[r + \frac{\alpha}{\rho}k^2\right]\left[\frac{\partial\mu}{\partial c}\right]_s \,, \tag{4.12}$$

$$r_< \approx \frac{1 + Dk^2\tau}{1 + D_T k^2\tau}\frac{\gamma}{\rho T}\left[\frac{\partial T}{\partial s}\right]_\mu k^2 \,. \tag{4.13}$$

As usual, the inverse susceptibilities are homogeneous functions of k and $\xi = \Lambda t^{-\nu}$. For example, $(\partial T/\partial s)_\mu$ is approximately $k^{2-\eta} f(k\xi)$; for $k\xi \gg 1$, it vanishes as $k^{2-\eta}$ and, for $k\xi \ll 1$, it vanishes as t^γ. The mode frequencies are displayed schematically in Fig. 1.

To lowest order in small quantities, the corresponding eigenvectors of M are

$$\begin{aligned} \mathbf{f}(k) &= (\ D_T k^2 \quad 1/\tau\ ) \quad \text{fast} \,, \\ \mathbf{s}(k) &= (\ \ 1 \quad 1/\eta\ ) \quad \text{slow} \,. \end{aligned} \tag{4.14}$$

As k crosses k_H, the fast eigenvector rotates in the $s-c$ plane—from the "heat direction" to the "concentration direction"; the slow eigenvector is roughly independent of k. Thus, the eigenvectors and eigenvalues show that the fast mode should be associated with chemistry, and the slow mode with heat, when $k \ll k_H$; the roles are reversed when $k_H \ll k$. Both modes become diffusive when $k_C \ll k$. For $k \approx k_H$, no clear separation is possible.

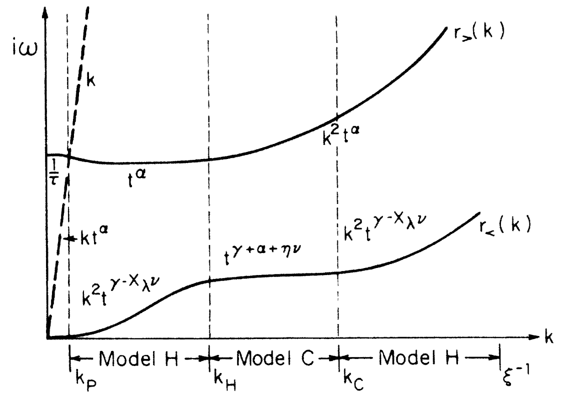

FIG. 1. The frequencies of the hydrodynamic modes as a function of wavenumber, k, and reduced temperature, t, for large coherence length, ξ (ξ must be large enough to violate the Ginzburg criterion for mean field behavior). Four wavenumber regimes, separated by the wavenumbers, k_P, k_H, and k_C (determined by the reaction rate, the thermal and particle diffusivities, and the sound velocity) are depicted *schematically*. The (real) frequency of sound wave modes is indicated by a dashed line. In each regime, the rate of the fastest mode is unaltered, and the rate of the next fastest is "weakly" reduced (as the inverse specific heat, t^{α}). Thus, the frequency of the mode $r_>(k)$ is "weakly" reduced for $k > k_P$, and the frequency of the "slow mode," $r_<(k)$, is drastically reduced for all k. The effects of critical dynamics, which alter the inverse susceptibility or Van Hove prediction, t^{γ}, for the temperature dependence of critical slowing, are indicated as are the models that apply in the three regions where chemical relaxation is relevant.

In particular, for $k_H \ll k \ll k_C$ we have

$$r_<(k) \approx r\left(\frac{\partial\mu}{\partial c}\right)_s\left(\frac{\partial T}{\partial s}\right)_\mu\left(\frac{\partial s}{\partial T}\right)_c = r\left(\frac{\partial\mu}{\partial c}\right)_T ,$$

$$r_>(k) \approx D_Tk^2 = \frac{\gamma}{\rho T}\left(\frac{\partial T}{\partial s}\right)_c k^2 , \tag{4.15}$$

i.e., a strongly suppressed chemical reaction rate and weakly suppressed heat diffusion, while for $k_P \ll k \ll k_H$ we have

$$r_<(k) \approx \frac{\gamma}{\rho T}\left(\frac{\partial T}{\partial s}\right)_\mu k^2 ,$$

$$r_>(k) \approx \frac{1}{\tau} = r\left(\frac{\partial\mu}{\partial c}\right)_s , \tag{4.16}$$

i.e., strongly suppressed heat diffusion and a weakly suppressed reaction rate.

In the $k \to 0$ macroscopic limit, in which transport coefficients are customarily defined, the simple arguments of the Introduction apply. In addition to macroscopic measurements in space and time, one can measure the time-dependence of spatially varying fluctuations of wavenumber k by light-scattering experiments involving a wavevector transfer $q = k$. Typically, q can range from 10^{-3} to $10^{-5}\,\text{cm}^{-1}$, and with "typical" values of τ, D, D_T (as above) one might hope to probe intermediate wave vectors. The dielectric structure factor measured in these experiments would show two superimposed Rayleigh peaks with widths given by the eigenmode frequencies (along with Brillouin peaks at sound-wave frequencies). We emphasize that such coherent scattering experiments are quite different from the incoherent photoexcitation experiments of Krichevskii *et al.* The latter probe fluctuations of vanishing wavenumber, not fluctuations with the wavenumber, q, of the impinging light.

This prediction of a suppressed reaction rate for values of k that satisfy $k_H \ll k \ll k_C$ is subject to further constraints. For example, it does not apply to a system that has more than two components and a single reaction, no matter how many components the reaction involves.[1] In an m-component system with one reaction, $m-1$ quantities are conserved. The system therefore has $m-2$ particle diffusion modes (in addition to the mass conservation mode that combines with momentum conservation to produce sound). In the reaction

$$\nu_1A_1 + \cdots \nu_iA_i \rightleftarrows \mu_1B_1 + \cdots \mu_kB_k, \quad i+k=m,$$

for example, the $(i-1)+(k-1)$ quantities

$$\frac{A_1}{\nu_1}-\frac{A_j}{\nu_j},\ \frac{B_1}{\mu_1}-\frac{B_j}{\mu_j}$$

are conserved. The $m-2$ modes associated with these conservation laws have frequencies $\omega_i \approx D_ik^2$ which are much slower than the reaction rate, $1/\tau$, when $k \ll k_C$. Consequently, for $k_H \ll k \ll k_C$, the appropriate reaction rate is

$$\frac{1}{\tau} \approx r\left(\frac{\partial\mu}{\partial c}\right)_{T,p,n_1,\ldots n_{m-2}} , \tag{4.17}$$

which is weakly suppressed for $m=3$ and regular for $m=4$. Related thermodynamic conditions, that follow from GW and lead to weaker singularities in multicomponent systems than PG predict, have been discussed by Wheeler and Petschek.[9]

V. RENORMALIZATION GROUP CORRECTIONS

The remainder of this paper summarizes briefly corrections to Van Hove theory and corrections to those corrections. We use a RG approach with an expansion in $\epsilon = 4-d$, so that we can compute $o(\epsilon)$ corrections to the slopes in Fig. 1.

As is well known, the Van Hove hypothesis (that the Onsager coefficients are "local" and regular as $\xi \to \infty$) does not hold in less than four dimensions. The nonlocality results from multiple scattering off long-lived fluctuations. Nonlinearities in $\delta F/\delta\psi$ in Eq. (3.6) and "mode-coupling" terms[10] arising from Poisson-bracket relations can both act to couple these fluctuations. Using well-established RG machinery,[11] we can compute, perturbatively in ϵ, response functions $R(k,\omega)$ and correlation functions $C(k,\omega)$ that have the requisite properties.

A straightforward application of the RG to the binary-system model quickly shows that in the "scaling limit," both k_H and k_C tend towards ∞ as they do in Model H of Siggia, Halperin, and Hohenberg.[4] In fact, the model behaves exactly like Model H in this limit, as we now show.

In general, we cannot diagonalize M and χ^{-1} with the same choice of variables. M is diagonalized by the transformation

$$\psi' = \Lambda\psi, \quad M' = \Lambda M \Lambda^{-1}, \quad \Lambda^{-1} = [\ \mathbf{f}(k)\ \ \mathbf{s}(k)\ ] \tag{5.1}$$

while χ^{-1} is diagonalized by the transformation discussed at length in Sec. IV. However, the eigenvector basis described above is equivalent to a change to the variables s and c_r for $k \ll k_H$ and to the variables c and s_r for $k \gg k_H$.

Thus, for $k \ll k_H$, we have a (slow) critical conserved heat mode and a (fast) noncritical nonconserved composition mode, with M and χ^{-1} both effectively diagonal. The system is therefore the same as Model B of Halperin, Hohenberg, and Ma[5] and has Van Hove dynamics. We next note, as in Ref. 4, that the coupling of the order parameter to the transverse part of the velocity is relevant. Its inclusion converts Model B to Model H. Thus, for $k \ll k_H$, we conclude that, as $\xi \to \infty$, the slow mode behaves as $r_<(k) \approx k^{4-\eta-x_\lambda}$ with $x_\lambda = 18\epsilon/19 + o(\epsilon^2)$. The dependence on ξ is given by scaling arguments, i.e., for $k \ll \xi^{-1}$, we have $r_< \approx k^2\xi^{-2+\eta+x_\lambda}$. In other words, the diffusion constant vanishes as $t^{\gamma-x_\lambda\nu}$, with $\gamma - x_\lambda\nu \approx 0.64$.

As $k \to k_H$, we accumulate "corrections to scaling"; the effect of the finite cutoff is to break "scale invariance" at large k.[12] Also, if the minimum ξ^{-1} attained in an experiment satisfies $\xi^{-1} \gtrsim k_H$, the Ginzburg criterion for the heat-velocity mode coupling will be satisfied and Van Hove or mean-field exponents observed.

We next consider the modes for $k_H \ll k \ll k_C$. Suppose that k_C is very large, i.e., that $k_C \approx \Lambda$, which is "infinite" for RG purposes. Then, for $k_H \ll k$, we have a (slow) critical nonconserved chemical relaxation mode and a (fast) noncritical conserved heat mode. In the limit $k_H \to 0$ the theory again has no scale and the RG can be applied—with the proviso that the scaling equation[11] may not be extended to values of $k \lesssim k_H$.

In this regime, the $q_r\psi^2$ term in the free energy gives rise to important couplings between order-parameter fluctuations and energy fluctuations. The critical dynamical properties of these modes are described by Model C. Simple power counting shows that the coupling of a nonconserved order parameter to the velocity is irrelevant above $d = 2$. Thus, for intermediate wavevectors, the results for Model C apply; at T_c, both roots have the same dependence

$$r_> \approx k^{2+\alpha/\nu} \text{ and } r_< \approx k^{2+\alpha/\nu}. \tag{5.2}$$

It then follows from scaling that the roots behave as $k^2\xi^{-\alpha/\nu}$ and $\xi^{-2-\alpha/\nu}$ when $k\xi \ll 1$. In other words, the chemical relaxation time constant vanishes strongly, as $t^{2\nu+\alpha}$, with $2\nu + \alpha = \gamma + \alpha + \eta\nu = 2 - \nu \approx 1.37$, while the thermal diffusivity vanishes weakly, as t^α. Note, incidentally, that in contrast with the small k regime, here (as in the stochastic Ising model) the inverse susceptibility or Van Hove critical exponent γ *underestimates* the rate of slowing.

These results are not exact since k_H/k_C is finite. We can neither take $k_H \to 0$ nor $k_C \to \infty$. As a result, asymptotic corrections to Eq. (5.2) cannot be obtained rigorously by straightforward RG procedures. In view of the difficulty of obtaining more accurate results and the limited utility such results would have, we have not pursued this analysis further.

The last regime to be considered is the one in which $\Lambda \gg k \gg k_C$. As the chemical reaction is "turned off," this regime grows until it covers all wavenumbers. In this regime, there are two diffusive modes, one of which is critically slowed. As $\xi \to \infty$, the same degrees of freedom approximately diagonalize both M and χ^{-1}, and the dynamical behavior of the pair of modes can be described by Model D. This model obeys Van Hove theory.[5] Once again, the coupling to the transverse velocity is relevant, and its inclusion leads to dynamics described by Model H. Thus, for $k \gg k_C$, as $\xi \to \infty$, we find

$$r_> \approx k^{2+\alpha/\nu} \text{ and } r_< \approx k^{4-\eta-x_\lambda}. \tag{5.3}$$

In other words, the diffusivity of the slow "concentration" mode vanishes as $t^{\gamma-x_\lambda\nu}$, and the diffusivity of the fast "heat" mode vanishes as t^α.

When $k \approx k_H$ and $k \approx k_C$ the situation is even less amenable to the RG than when $k_H \ll k \ll k_C$. Nonetheless, an interpolation formula which joins the corrected versions of the curves in Fig. 1 should give adequate predictions for foreseeable experiments.

More than a year ago, a preprint of this paper was circulated and submitted for publication. In that version, we reported the same qualitative conclusions we report here. When it was suggested that speedy publication was not warranted we decided to postpone submission until the RG analysis was performed. During the past year, Greer[13] has redone the experiment reported by Krichevskii *et al.*, and demonstrated that the chemical relaxation rate of spatially uniform composition fluctuations is not drastically reduced. She finds, in qualitative agreement with our analysis, that the critically slowed mode is associated with heat transport. However, Greer finds that its critical slowing is better fit by a thermal diffusivity proportional to the reduced temperature t than by one proportional to $t^{\nu(2-x_\lambda-\eta)} \approx t^{0.64}$. Our calculations confirm the latter prediction near the critical point. We have no explanation for the remaining discrepancy—a discrepancy that she reports has also been observed in *some* nonreacting samples. If the discrepancy persists, we believe it will have to be attributed to the fact that the experiment has not measured the temperature dependence of the rate of thermal diffusion near T_c. For example, if experiments were performed at reduced temperatures t small enough for slowing to be detected but large enough for the Ginzburg criterion to be satisfied, neither static nor dynamic RG corrections to mean field would be observed and the rate of thermal diffusivity would decrease as $t^{\gamma_{\mathrm{MFT}}}$ with $\gamma_{\mathrm{MFT}} = 1$.

In addition, hope persists that a scattering experiment can be performed that probes the relaxation times of fluctuations with wavenumbers that lie between k_C and k_H. In such an experiment, the relaxation time should grow approximately as $t^{-1.37}$.

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