

Dynamical critical phenomena in chemically reactive fluid mixtures

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It is shown that the interplay between chemical reactions and thermodynamic stability gives rise to some novel phenomena manifested in a slowing down of the chemical reaction and in changes in the critical behavior of transport processes. In an n -component fluid, when all the components participate in the reaction, the rate vanishes near the critical point T_c as $[(T - T_c)/T_c]^\gamma$, where $\gamma \sim 1.25$. When one of the components does not participate in the reaction, the rate vanishes, in general, as $[(T - T_c)/T_c]^\alpha$, where $\alpha \sim 0.12$. If more than one component is nonreactive the rate of the reaction is not sensitive to the approach to T_c . Reactive binary mixtures are treated in detail on the basis of a mode-coupling theory. In contrast to nonreactive mixtures, the shear viscosity has no divergence near the critical point. In addition, the diffusion coefficient has a different temperature and wave-vector dependence.

I. INTRODUCTION

The aim of this paper is to investigate the critical behavior of dynamical phenomena that occur in chemically reactive fluid systems near the thermodynamic critical points. Of prime interest to us is the possibility of the slowing down of chemical reactions in such systems; however, the influence of the existence of a chemical reaction on the critical behavior of transport processes (diffusion, viscosity, etc.) is also interesting.

The fact that a critical slowing down of chemical reactions should be expected, can be established using a simple argument based on the "conventional theory" of slowing down.¹ Consider an example of a binary mixture of dimers and monomers in which the reaction $B_2 \rightleftharpoons 2B$ takes place. As is well known,² for small deviations from equilibrium the observed reaction rate (i.e., the net difference between the forward and backward reactions) is proportional to the affinity A defined by

$$A \equiv - \sum \nu_i \mu_i. \quad (1.1)$$

Here μ_i are the chemical potentials and ν_i are the stoichiometric coefficients in the reaction. For the reaction considered here $A = 2\mu_B - \mu_{B_2}$. Defining the extent of advancement of the reaction ξ according to $\nu_i d\xi = dN_i$, where N_i are the number of particles of the i th species, we thus have

$$\frac{d\xi}{dt} = rA \quad (1.2)$$

for small deviations of ξ from equilibrium. r is a proportionality constant which contains microscopic information. Since the affinity vanishes at equilibrium,² we expand A in ξ and get, for con-

stant thermodynamic parameters,

$$\frac{d\xi}{dt} = r \left(\frac{dA}{d\xi} \right)_{\text{eq}} (\xi - \xi_{\text{eq}}) \quad (1.3)$$

to linear order. The subscript eq reminds us that the thermodynamic derivative is calculated in equilibrium. The crux of our argument is that the thermodynamic derivative in Eq. (1.3) vanishes near the critical point of a system like this B_2 , B binary mixture. In fact, we shall show below that the derivative $\partial A / \partial \xi$ vanishes at the critical point of any system of n components, in which all n (or $n - 1$) components participate in the same reaction. Thus, assuming that r has no critical anomaly, slowing down of the reaction can be predicted. An interesting point is that the way in which the slowing down is manifested is expected to be universal. Independently of the nature of the chemical constituents, when all of them participate in the chemical reaction, the derivative $(\partial A / \partial \xi)$ vanishes in the same way, i.e., $(\partial A / \partial \xi) \propto [(T - T_c)/T_c]^\gamma$ where γ is a critical index ($\gamma \sim 1.25$), T is the temperature, and T_c is the critical temperature. When $n - 1$ components react and one component is nonreactive, the rate of reaction vanishes generally as $[(T - T_c)/T_c]^\alpha$, where α is another critical index ($\alpha \sim 0.12$).

Evidently, the relation embodied in Eq. (1.2) rests on linear theory. It thus becomes very important to assess the role of the nonlinearities and how they affect the relaxation times. This is one of the major aims of this paper.

In fact, it seems that the phenomena of critical slowing down of chemical reactions had been observed experimentally many years ago by Krichevskii and co-workers.³ Two experiments were reported; in the first, a mixture of CO_2 and I_2 was irradiated with light to dissociate the I_2 into

atoms, and the recombination rate was measured. In the second, pure Cl_2 was used and a similar experiment performed. In both cases it was found that the recombination rate was dramatically slowed (one to two orders of magnitude) when the system was kept near its critical (liquid-gas) point.

Surprisingly, these findings were never properly interpreted in the context of modern theories of critical phenomena. Originally, Krichevskii *et al.* attributed the effect to slowing down in diffusion. This view has been criticized by Leontovich,⁴ who, however, did not suggest a proper counter explanation. In a recent communication⁵ we have attempted an explanation which is based on the above-mentioned relation between reaction rates and thermodynamic quantities. In this paper we elaborate on this theory and supplement it with a discussion on the influence of chemical reactions on transport processes.

In Sec. II of this paper we present the thermodynamic considerations which establish the fact that $\partial A/\partial \xi \rightarrow 0$ at the critical point. In Sec. III we present a linear hydrodynamic theory of a reactive binary mixture, with the aim of showing that in the vicinity of a critical point the composition mode indeed slows down with an eigenvalue proportional to $(\partial A/\partial \xi)_{P,T}$ (where P and T are the pressure and the temperature). In Sec. IV we depart from linear approximations and consider a mode-coupling theory^{6,7} of the problem. It is shown there that the critical slowing down of the chemical reaction is not affected by the mode-coupling nonlinearities. On the other hand we argue that the transport coefficients are affected by the existence of the chemical reaction, and that the weak divergence of the viscosity, which is observed⁶⁻⁸ in nonreactive binary mixtures, is predicted to disappear in this case. The effects on the diffusion constant are also calculated. In Sec. V we offer a summary of the novel findings, a discussion of the physics of the phenomenon, and some concluding remarks.

II. THERMODYNAMIC ANALYSIS

In this section we show that the thermodynamic derivative $(\partial A/\partial \xi)_{P,T}$ [or $(\partial A/\partial \xi)_{P,T,\mu}$] vanishes at the critical point of any multicomponent mixture in which all components (or all but one) participate in a chemical reaction. In all cases we consider a single uniform phase and the approach to a critical point (or critical line) where the uniform phase becomes unstable. Thus the vanishing of $(\partial A/\partial \xi)_{P,T}$ [or $(\partial A/\partial \xi)_{P,T,\mu}$] will be seen to signal the loss of stability.^{9,10} The case in which all components participate in the reaction is simpler and would be treated first.

A. All components participate in the reaction

Consider the Gibbs free energy $G(P, T, N_1, \dots, N_n)$ and its differential which is written generally as

$$dG = -SdT + VdP + \sum_{i=1}^n \mu_i dN_i \quad (2.1)$$

for an n -component system. Since all components participate in the reaction (written symbolically as $\sum \nu_i M_i = 0$), the differentials dN_i are all related to the extent of reaction ξ via $\nu_i d\xi = dN_i$. Since $A = -\sum_i \nu_i \mu_i$ we have

$$dG = -SdT + VdP - Ad\xi. \quad (2.2)$$

The condition for a stable equilibrium is that G is a minimum at constant P and T . Thus the conditions

$$\left(\frac{\partial G}{\partial \xi}\right)_{P,T} = -A(P, T, \xi) = 0, \quad (2.3)$$

$$\left(\frac{\partial^2 G}{\partial \xi^2}\right)_{P,T} = -\left(\frac{\partial A}{\partial \xi}\right)_{P,T} > 0, \quad (2.4)$$

are the necessary and sufficient conditions for stability at constant P and T . It can be shown on general grounds that Eq. (2.4) determines, in fact, the stability of the system. The breakdown of this condition appears always before the loss of stability due to other types of perturbations (say for constant V, S etc.).⁹

Equation (2.3) determines ξ as a function of the thermodynamic parameters. Thus the number of degrees of freedom in this system is the same as in a pure one-component fluid. Such a system would have an isolated critical point, which, being at the boundary of stability, is determined by the relations^{9,10}

$$\left(\frac{\partial A}{\partial \xi}\right)_{P,T} = \left(\frac{\partial^2 A}{\partial \xi^2}\right)_{P,T} = 0. \quad (2.5)$$

The critical indices will be those of a pure fluid, namely,

$$\left(\frac{\partial A}{\partial \xi}\right)_{P,T} \sim \left(\frac{T - T_c}{T_c}\right)^\gamma, \quad (2.6)$$

where γ is a critical index ($\gamma \sim 1.25$).

In addition to the temperature dependence of $(\partial A/\partial \xi)$, we shall need below the temperature dependence of the specific heats of a reactive mixture. One has to distinguish between the specific heat at constant concentration, $C_{P,\xi}$, and the specific heat at chemical equilibrium, $C_{P,A=0}$. These two quantities are related by the thermodynamic formula

$$C_{P,A} = C_{P,\xi} - \frac{h^2}{T \left(\frac{\partial A}{\partial \xi}\right)_{T,P}}. \quad (2.7)$$

Here h is the heat of reaction at constant T and P . In Eq. (2.7) and hereafter we write $C_{P,A}$ for

$C_{P,A=0}$.

A standard thermodynamic argument leads to the conclusion that

$$C_{P,A} \sim \left(\frac{\partial V}{\partial P}\right)_{T,A} \sim \left(\frac{\partial A}{\partial \xi}\right)_{P,T}^{-1} \sim \left(\frac{T-T_c}{T_c}\right)^{-\gamma}. \quad (2.8)$$

On the other hand, $C_{P,t}$ has a weaker singularity:

$$C_{P,t} \sim \left(\frac{T-T_c}{T_c}\right)^{-\alpha}, \quad (2.9)$$

where α is a critical index ($\alpha \approx 0.12$).

B. $n-1$ components participate in the reaction

In this case we separate the nonreactive component and designate it with a subscript zero:

$$dG = -SdT + Vdp + \mu_0 dN_0 - Ad\xi,$$

where again we used the fact that $dN_i = \nu_i d\xi$ for the reactive components. The additional degree of freedom N_0 leads to the existence of a critical line rather than an isolated critical point.

From the general theory of bilinear forms it follows that the stability conditions in this case are^{9,10}

$$\left(\frac{\partial \mu_0}{\partial N_0}\right)_{P,T,t} > 0, \quad \left(\frac{\partial A}{\partial \xi}\right)_{P,T,N_0} < 0, \quad (2.10a)$$

and

$$\Delta \equiv \begin{vmatrix} \left(\frac{\partial \mu_0}{\partial N_0}\right)_{P,T,t} & -\left(\frac{\partial A}{\partial N_0}\right)_{P,T,t} \\ \left(\frac{\partial \mu_0}{\partial \xi}\right)_{P,T,N_0} & -\left(\frac{\partial A}{\partial \xi}\right)_{P,T,N_0} \end{vmatrix} \geq 0. \quad (2.10b)$$

The conditions (2.10) can be simplified, however, by using the thermodynamic relation

$$\left(\frac{\partial A}{\partial \xi}\right)_{P,T,\mu} = \left(\frac{\partial A}{\partial \xi}\right)_{P,T,N_0} + \frac{\left(\frac{\partial A}{\partial N_0}\right)_{P,T,t}^2}{\left(\frac{\partial \mu_0}{\partial N_0}\right)_{P,T,t}}. \quad (2.11)$$

Using Eq. (2.11) and the fact that $(\partial \mu_0 / \partial \xi) = (\partial A / \partial N_0)$, the determinant (2.10b) can be written as

$$\Delta = -\left(\frac{\partial \mu_0}{\partial N_0}\right)_{P,T,t} \left(\frac{\partial A}{\partial \xi}\right)_{P,T,\mu} \geq 0. \quad (2.12)$$

The latter condition is met only if $(\partial A / \partial \xi)_{P,T,\mu} < 0$. By comparing Eqs. (2.10), (2.11), and (2.12), it is seen that this condition is violated before either of the conditions (2.10a). Thus the boundary of stability is determined by the vanishing of $(\partial A / \partial \xi)_{P,T,\mu}$. At the critical line

$$\left(\frac{\partial A}{\partial \xi}\right)_{P,T,\mu} = \left(\frac{\partial^2 A}{\partial \xi^2}\right)_{P,T,\mu} = 0. \quad (2.13)$$

In this case, again, the temperature dependence of the derivative $(\partial A / \partial \xi)_{P,T,\mu}$ is determined by the strong singularity^{11,12}:

$$\left(\frac{\partial A}{\partial \xi}\right)_{P,T,\mu} \sim \left(\frac{T-T_c}{T_c}\right)^\gamma. \quad (2.14)$$

The derivative $(\partial A / \partial \xi)_{P,T,N_0}$ vanishes according to the weak dependence^{11,12}

$$\left(\frac{\partial A}{\partial \xi}\right)_{P,T,N_0} \sim \left(\frac{T-T_c}{T_c}\right)^\alpha. \quad (2.15)$$

Notice that in this case, contrary to the previous one, there are two distinct thermodynamic derivatives $(\partial A / \partial \xi)$. Later we shall argue that although $(\partial A / \partial \xi)_{P,T,\mu}$ determines the boundary of stability, it is $(\partial A / \partial \xi)_{P,T,N_0}$ which determines the chemical reaction time scale. Thus in the case of $(n-1)$ reactive components we expect a weaker slowing down of the reaction. In the more general case of $(n-2)$ or more nonreactive components, no critical slowing down of the chemical reaction is expected. There the chemical rate is related to $(\partial A / \partial \xi)_{P,T,N_1,N_2,\dots}$, and such a derivative is expected to be finite near the boundary of stability.^{11,12}

III. LINEAR HYDRODYNAMICS

In this section we utilize the information gained in the previous section to study the mode structure of a reactive fluid mixture near its critical point. Firstly, we limit the discussion to a binary mixture. The major aim is to show that near the critical point the composition relaxes as a mode with a characteristic time that diverges like $[(T-T_c)/T_c]^{-\gamma}$. At the end of the section we discuss briefly the slowing down in the case of ternary mixtures.

A. Linearized equations of motion in binary systems

The linearized hydrodynamic equations can be obtained as a straightforward generalization of the equations of motion of a nonreactive binary mixture. In fact, the quantity μ , defined by, say, Landau and Lifshitz¹³ as $\mu_1/m_1 - \mu_2/m_2$ where m_1 and m_2 are the molecular masses of the components, would be exactly proportional to the affinity in this case. The reason is that whatever the reaction between two components is, the stoichiometric coefficients are inversely proportional to the molecular masses of the species. Thus we may choose the mass fraction of one component as the progress variable (to be denoted again by ξ) and write¹⁴

$$\frac{\partial \rho}{\partial t} + \rho \vec{\nabla} \cdot \vec{v} = 0, \quad (3.1)$$

$$\rho \frac{\partial \vec{\nabla} \cdot \vec{v}}{\partial t} = -\nabla^2 P + \left(\frac{4}{3}\eta + \eta_v\right) \nabla^2 \vec{\nabla} \cdot \vec{v}, \quad (3.2)$$

$$\frac{\partial \xi}{\partial t} = D \left(\nabla^2 \xi + \frac{k_T}{T} \nabla^2 T + \frac{k_P}{P} \nabla^2 P \right) + rA, \quad (3.3)$$

$$\begin{aligned} \frac{\partial S}{\partial t} = & \frac{\lambda}{\rho T} \nabla^2 T + \frac{Dk_T}{T} \left(\frac{\partial A}{\partial \xi} \right)_{P,T} \left(\nabla^2 \xi + \frac{k_P}{P} \nabla^2 P \right) \\ & + \left(\frac{\partial S}{\partial \xi} \right)_{P,T} D \left(\nabla^2 \xi + \frac{k_P}{P} \nabla^2 P + \frac{k_T}{T} \nabla^2 T \right). \end{aligned} \quad (3.4)$$

Here ρ , \vec{v} , η , η_v , D , λ , and k_T are the density, velocity field, shear and bulk viscosities, diffusion constant [$D \equiv \alpha(\partial A/\partial \xi)_{P,T}$], heat conductivity, and the thermodiffusion constant, respectively. The quantity k_P/P is thermodynamic and equals $(\partial A/\partial P)_{T,\xi}/(\partial A/\partial \xi)_{T,P}$.

Notice that the chemistry term rA appears only in (3.3) and not in (3.4). The reason is that the chemical reaction contributes only quadratic terms to the entropy production.² Since A vanishes at equilibrium, we expand A in P, T and ξ :

$$rA = r \left(\frac{\partial A}{\partial \xi} \right)_{P,T} \delta \xi + r \left(\frac{\partial A}{\partial T} \right)_{\xi,P} \delta T + r \left(\frac{\partial A}{\partial P} \right)_{\xi,T} \delta P. \quad (3.5)$$

By using obvious thermodynamic identities Eq. (3.5) can be written in the form¹⁴

$$rA = -\frac{1}{\tau_{T,P}} \left[\delta \xi - \left(\frac{\partial \xi}{\partial T} \right)_{P,A} \delta T - \left(\frac{\partial \xi}{\partial P} \right)_{T,A} \delta P \right], \quad (3.6)$$

where $\tau_{T,P} \equiv (1/r)(\partial A/\partial \xi)_{T,P}^{-1}$.

Equations (3.1)–(3.4) are written in terms of variables that are not statistically independent. For studying critical behavior it is advantageous to work with variables that are both normalized and statistically independent in the sense of static correlation functions. We thus construct a set of variables $\{\beta\}$ such that $\langle \beta_{\vec{k}}^i \beta_{-\vec{k}}^j \rangle = \delta_{ij}$. The variables are¹⁴

$$\beta_{\vec{k}}^1(t) = \left(\frac{\rho}{k_B V C_{P,\xi}} \right)^{1/2} \delta \tilde{S}_{\vec{k}}(t), \quad (3.7a)$$

$$\beta_{\vec{k}}^2(t) = \left[\frac{\rho}{k_B V T} \left(\frac{\partial A}{\partial \xi} \right)_{P,T} \right]^{1/2} \delta \xi_{\vec{k}}(t), \quad (3.7b)$$

$$\beta_{\vec{k}}^3(t) = \left(\frac{\chi_{S,\xi}}{k_B V T} \right)^{1/2} \delta P_{\vec{k}}(t), \quad (3.7c)$$

$$\beta_{\vec{k}}^4(t) = \left(\frac{\chi_{S,\xi}}{k_B V T} \right)^{1/2} (\vec{\nabla} \cdot \vec{v})_{\vec{k}}(t), \quad (3.7d)$$

and in Eq. (3.7a),

$$\delta \tilde{S} = \delta S - \left(\frac{\partial S}{\partial \xi} \right)_{P,T} \delta \xi. \quad (3.7e)$$

Constructing the equation of motion for $\delta \tilde{S}$ from (3.4) and (3.3), Fourier transforming the resulting equations, and using the definitions (3.7), one gets a four by four matrix denoted by $\underline{K}(\vec{k})$ such that

$$\frac{\partial \{\beta_{\vec{k}}(t)\}}{\partial t} = \underline{K}(\vec{k}) \{\beta_{\vec{k}}(t)\}. \quad (3.8)$$

The matrix $\underline{K}(\vec{k})$ is given in Ref. 14 and is not reproduced here. For studying critical phenomena we are interested only in the small- k limit of $\underline{K}(\vec{k})$. Asymptotically close to the critical point, the correlation length $\xi \rightarrow \infty$. Therefore we first study the case $k = \xi^{-1} \rightarrow 0$. Then the matrix \underline{K} simplifies to a 3×3 matrix:

$$\begin{pmatrix} \gamma_T \tau_{T,P}^{-1} & -\tau_{T,P}^{-1} \gamma_T^{1/2} & C_2 \tau_{T,P}^{-1} \\ -\tau_{T,P}^{-1} \gamma_T^{1/2} & \tau_{T,P}^{-1} & C_4 \tau_{T,P}^{-1} \\ C_2 \tau_{T,P}^{-1} & C_4 \tau_{T,P}^{-1} & r_M \frac{C_{P,A}}{C_{P,\xi}} \tau_{T,P}^{-1} \end{pmatrix}, \quad (3.9)$$

where

$$\gamma_T \equiv \frac{C_{P,A} - C_{P,\xi}}{C_{P,\xi}},$$

$$C_2 \equiv \left(\frac{\rho}{T \chi_{S,\xi} C_{P,\xi}} \right)^{1/2} \left(\frac{\partial S}{\partial \xi} \right)_{P,T}$$

$$\times T \left[\left(\frac{\partial \xi}{\partial T} \right)_{P,A} \frac{\alpha_T T}{\rho C_{P,\xi}} + \left(\frac{\partial \xi}{\partial P} \right)_{T,A} \right], \quad (3.10)$$

$$C_4 \equiv - \left(\frac{\partial A}{\partial \xi} \right)_{P,T}^{1/2} \left[\left(\frac{\partial \xi}{\partial T} \right)_{P,A} \frac{\alpha_T T}{\rho C_{P,\xi}} + \left(\frac{\partial \xi}{\partial P} \right)_{T,A} \right],$$

where $\alpha_T \equiv (1/\rho)(\partial \rho/\partial T)_{P,\xi}$, and $\chi_{S,\xi} = (1/\rho)(\partial \rho/\partial P)_{S,\xi}$.

By solving the cubic equation for the eigenvalues of the matrix (3.9) one can easily find that in this case the eigenvalues are proportional to $[(T - T_c)/T_c]^r$, $[(T - T_c)/T_c]^\alpha$, and to unity, respectively. However, for most experimentally accessible situations, ξ is never greater than, say, 10^5 cm. Thus we need to study the regime $k \gtrsim 10^5$ cm⁻¹. The analytic evaluation of the eigenvalues of \underline{K} with its full k dependence is cumbersome. We thus limit the analysis to cases where the following conditions are met:

$$\frac{\lambda}{\rho C_{P,\xi}} k^2 \ll k C_\infty, \quad D k^2 \ll k C_\infty, \quad (3.11)$$

$$\frac{1}{\rho} \left(\frac{4}{3}\eta + \eta_v \right) k^2 \ll k C_\infty,$$

and

$$\tau_{T,P}^{-1} \ll k C_\infty, \quad (3.12)$$

where $C_\infty^2 = (\partial P/\partial \rho)_{S,\xi}$.

The conditions (3.11) are always met for k 's of the order of ξ^{-1} . The condition (3.12), however, means that the chemical reaction cannot be too fast. As shown before,¹⁴ the eigenvalues can be now obtained by factorizing \underline{K} into two blocks. The variables β_{ξ}^3 and β_{ξ}^4 couple to yield two propagating modes that decay on the time scale of sound. Thus these are immaterial for critical dynamics. The two variables β_{ξ}^1 and β_{ξ}^2 couple to

yield two nonpropagating modes. Writing

$$\frac{d}{dt} \begin{pmatrix} \beta_{\xi}^1(t) \\ \beta_{\xi}^2(t) \end{pmatrix} = -\underline{K}^I \begin{pmatrix} \beta_{\xi}^1(t) \\ \beta_{\xi}^2(t) \end{pmatrix}, \quad (3.13)$$

it can be easily shown that¹⁴

$$\underline{K}^I = \begin{pmatrix} \frac{\lambda}{\rho C_{P,\xi}} k^2 + \gamma_T \tau_{T,P}^{-1} & k_T D \left[\frac{1}{TC_{P,\xi}} \left(\frac{\partial A}{\partial \xi} \right)_{P,T} \right]^{1/2} k^2 - \gamma_T^{1/2} \tau_{T,P}^{-1} \\ k_T D \left[\frac{1}{TC_{P,\xi}} \left(\frac{\partial A}{\partial \xi} \right)_{P,T} \right]^{1/2} k^2 - \tau_{T,P}^{-1} \gamma_T^{1/2} & D k^2 + \tau_{T,P}^{-1} \end{pmatrix}. \quad (3.14)$$

B. Separation into heat and composition modes for $k \sim \xi^{-1}$

One simple case can be immediately investigated. This is the case of a thermoneutral reaction. Here h of Eq. (2.7) is zero and, respectively, $\gamma_T = 0$. Near the critical point the remaining part of the off-diagonal elements of \underline{K}^I vanish proportionally to $[(T - T_c)/T_c]^{(3\gamma + \alpha)/2}$. Thus the composition becomes a normal mode and relaxes like

$$\xi(t) = e^{-(Dk^2 + \tau_{T,P}^{-1})t} \xi(0).$$

More generally, when $\gamma_T \neq 0$, the term proportional to k^2 in the nondiagonal terms is asymptotically negligible compared to $\tau_{T,P}^{-1} \gamma_T^{1/2}$ which is proportional to $[(T - T_c)/T_c]^{(\gamma + \alpha)/2}$.

Taking this into account, one can establish¹⁴ that for k values that obey

$$k > \left(\frac{\gamma_T}{(\lambda/\rho C_{P,\xi} - D)\tau_{T,P}} \right)^{1/2}, \quad (3.15)$$

the eigenvalues can be again approximated by the diagonal terms of Eq. (3.14). Analyzing the quantities appearing in Eq. (3.15) one sees that the critical divergencies cancel in the right-hand side of the inequality. We thus estimate the range of k values which obey Eq. (3.15) at noncritical conditions. Picking $\lambda/\rho C_{P,\xi} \sim 10^{-2}$ cm²/sec, $\gamma_T \sim 0(1)$, $D \ll \lambda/\rho C_{P,\xi}$, and $\tau_{T,P} \sim 10^{-6}$ sec, we find that k 's that are greater than 10^4 cm⁻¹ obey this inequality. As argued before, k is rarely smaller than 10^5 cm⁻¹, and therefore this condition is easily satisfied. If, on the other hand, the chemical reaction time scale is extremely fast (i.e., much faster than a microsecond) the condition (3.12) can be violated and then the previous analysis ($k \rightarrow 0$) should be applied.

In conclusion, for a wide spectrum of problems

we can assume that the composition mode in a reactive binary mixture slows down according to the index γ near the critical point. For the analysis of the mode-coupling theory we shall write

$$\langle \xi_k(t) \xi_{-k} \rangle = e^{-(Dk^2 + \tau_{T,P}^{-1})t} \langle \xi_k \xi_{-k} \rangle. \quad (3.16)$$

C. Ternary and multicomponent mixtures

As an example for systems in which not all components participate in the reaction, we mention here a ternary mixture in which two components react. The linearized hydrodynamic equation can be written similarly to the case of binary mixtures.¹⁵ The major difference is that the characteristic time for the chemical reaction is¹⁵

$$\tau^{-1} = \gamma \left(\frac{\partial A}{\partial \xi} \right)_{P,T,N_0}. \quad (3.17)$$

Only this "chemical" time can appear in the eigenvalues of the hydrodynamic matrix. Indeed, for some limiting cases (dilute nonreactive or dilute two-reactive species) it can be shown analytically that the chemical relaxation time appears in the eigenvalues. Therefore, any slowing down of the chemical reaction can appear only with the rather weak singularity according to Eq. (2.15).

As mentioned before, if more than one component does not react, the characteristic "chemical" time will be of the form

$$\tau^{-1} = \gamma \left(\frac{\partial A}{\partial \xi} \right)_{P,T,N_1,N_2,\dots}. \quad (3.18)$$

According to the general theory of singularities in many-component systems, such a derivative has no anomaly near the critical surface.^{11,12}

The above discussion of the critical behavior of chemical relaxation times is not applicable to some special cases. Near special points of phase

diagrams such as azeotropes or extremal points on the critical line, the singularities are stronger and special considerations are called for.^{11,12}

IV. MODE-COUPLING ANALYSIS

In this section we assess the nonlinear mode-coupling contributions to the critical dynamics. The three quantities under investigation here are ν , the microscopic part of the chemical relaxation time [$\tau_{\mathbf{r},\mathbf{p}}^{-1} = \nu(\partial A/\partial \xi)_{\mathbf{p},\mathbf{r}}$], D , the diffusion constant, and η , the shear viscosity. We wish to see whether ν has any nonlinear critical anomaly and what the implications of the chemistry are on the usually calculated⁶⁻⁸ divergencies in α [$D = \alpha(\partial A/\partial \xi)_{\mathbf{p},\mathbf{r}}$] and η . We start the analysis with some microscopic considerations and then proceed to actual calculations.

A. Microscopic considerations

Microscopically, the variable of most interest in this problem is the number density of one of the components, say component α ⁷:

$$n_{\mathbf{h}}^{\alpha} = \sum_{i=1}^{N_{\alpha}} e^{i\mathbf{k}\cdot\mathbf{r}_i}, \quad (4.1)$$

where N_{α} is the number of molecules of species α at some instant. The equation of motion of $n_{\mathbf{h}}^{\alpha}(t)$ is

$$\begin{aligned} \frac{\partial}{\partial t} n_{\mathbf{h}}^{\alpha}(t) &= \frac{i\mathbf{k}}{m} \cdot \sum_{j=1}^{N_{\alpha}} \pi_j e^{i\mathbf{k}\cdot\mathbf{r}_j} + \gamma_{\mathbf{h}}^{\alpha}(t) \\ &= \frac{i\mathbf{k}}{m} \cdot \vec{g}_{\mathbf{h}}^{\alpha}(t) + \gamma_{\mathbf{h}}^{\alpha}(t). \end{aligned} \quad (4.2)$$

The quantity $\gamma_{\mathbf{h}}(t)$ arises from the rate of change of N_{α} due to the chemical reaction. It cannot be written in a model-independent form.¹⁶ We shall not need, however, its explicit form but only its symmetry properties.

Guided by the analysis of the previous section, we shall neglect some of the variables that, generally speaking, should be taken into account. Thus we shall neglect the total number density and the longitudinal component of momentum density, since these couple to give rise to sound modes that decay rapidly. We limit ourselves to conditions that meet the discussion of Sec. III B and we omit the energy density, as is most commonly done. Thus the only variables to be considered, besides $n_{\mathbf{h}}^{\alpha}(t)$, are the transverse components of the momentum density $\vec{g}_{\mathbf{h}}(t)$,

$$\vec{g}_{\mathbf{h}}(t) = \sum_{i=1}^N \pi_i e^{i\mathbf{k}\cdot\mathbf{r}_i}. \quad (4.3)$$

Choosing \vec{k} to be parallel to the z axis, we are then concerned with $g_{\mathbf{h}}^x(t)$ and $g_{\mathbf{h}}^y(t)$.

Denoting now by $\langle \rangle$ an equilibrium ensemble av-

erage, we define the following correlation function:

$$\langle \vec{j}_{\mathbf{h}}(t) \vec{j}_{-\mathbf{h}}(t) \rangle = \langle [e^{(1-P_L)t} (1-P_L) \vec{j}_{\mathbf{h}}] (1-P_L) \vec{j}_{-\mathbf{h}} \rangle, \quad (4.4)$$

where P_L is the projection operator onto the space of the "slow" variables $\mathcal{G}_{\mathbf{h}}$,

$$P_L \mathcal{G}_{\mathbf{h}} \equiv \langle \mathcal{G}_{\mathbf{h}} \mathcal{G}_{-\mathbf{h}} \rangle \langle \mathcal{G}_{\mathbf{h}} \mathcal{G}_{-\mathbf{h}} \rangle^{-1} \mathcal{G}_{\mathbf{h}}, \quad (4.5)$$

and $\vec{j}_{\mathbf{h}}$ is any variable; $i\mathcal{L}$ is the Liouvillian.

It is now straightforward to write down the microscopic definitions of the quantities D , η , and ν ^{7,16}:

$$D = \lim_{\mathbf{h} \rightarrow 0} \int_0^{\infty} dt \langle g_{\mathbf{h}}^x(t) g_{-\mathbf{h}}^x(t) \rangle \chi_{\mathbf{h}}^{-1}, \quad (4.6)$$

$$\eta = \lim_{\mathbf{h} \rightarrow 0} \int_0^{\infty} dt \langle \dot{g}_{\mathbf{h}}^y(t) \dot{g}_{-\mathbf{h}}^y(t) \rangle / k^2 \langle g_{\mathbf{h}}^y g_{-\mathbf{h}}^y \rangle, \quad (4.7)$$

$$\nu = \lim_{\mathbf{h} \rightarrow 0} \int_0^{\infty} dt \langle \gamma_{\mathbf{h}}(t) \gamma_{-\mathbf{h}}(t) \rangle, \quad (4.8)$$

and

$$\chi_{\mathbf{h}}^{\alpha} = \langle n_{\mathbf{h}}^{\alpha} n_{-\mathbf{h}}^{\alpha} \rangle. \quad (4.9)$$

In the mode-coupling theory, one recognizes that,¹⁷ while $(1-P_L)j_{\mathbf{h}}(t)$ is orthogonal to $\mathcal{G}_{\mathbf{h}}$ in the sense that $\langle (1-P_L)j_{\mathbf{h}}(t) A_{-\mathbf{h}} \rangle = 0$, we may form a set of bilinear variables $A_{\mathbf{h},\mathbf{h}'} A_{-\mathbf{h},-\mathbf{h}'}$ which do not have to be orthogonal to $(1-P_L)j_{\mathbf{h}}$. Since $A_{\mathbf{h}}$ is slowly varying for small \mathbf{k} , $A_{\mathbf{h},\mathbf{h}'} A_{-\mathbf{h},-\mathbf{h}'}$ will also be slowly varying if \mathbf{k} and \mathbf{k}' are sufficiently small. Thus we may write¹⁷

$$\begin{aligned} (1-P_L)j_{\mathbf{h}} &= [(1-P_L)j_{\mathbf{h}}]^{m1c} \\ &+ \sum_{\mathbf{h}'}^{k_c} \frac{\langle (1-P_L)j_{\mathbf{h}} \mathcal{G}_{-\mathbf{h}'} \mathcal{G}_{\mathbf{h}'} \rangle}{\langle (\mathcal{G}_{\mathbf{h},\mathbf{h}'} \mathcal{G}_{-\mathbf{h},-\mathbf{h}'})^2 \rangle} \mathcal{G}_{\mathbf{h},\mathbf{h}'} \mathcal{G}_{-\mathbf{h},-\mathbf{h}'}, \end{aligned} \quad (4.10)$$

where \vec{k}_c is a cutoff vector such that $\mathcal{G}_{\mathbf{h},\mathbf{h}'} \mathcal{G}_{-\mathbf{h},-\mathbf{h}'}$ is no longer slowly varying for $\vec{k}' > \vec{k}_c$. In Eq. (4.10) we ignore trilinear and higher nonlinear contributions. The quantity $[(1-P_L)j_{\mathbf{h}}]^{m1c}$ is the microscopic or rapidly decaying part of $(1-P_L)j_{\mathbf{h}}$ and it gives rise to the "bare" transport coefficients. Equation (4.10) can be used in Eqs. (4.6) to (4.8) to assess the mode-coupling contributions to the transport coefficients.

B. The chemical rate ν

Using Eq. (4.2) we see that the quantity $\gamma_{\mathbf{h}}$, be it as it may, must be odd under time reversal. This is an immediate consequence of the fact that $n_{\mathbf{h}}^{\alpha}$ is even under time reversal. In addition, it must be even under parity.¹⁶ These two properties mean that its correlation function with any of our dynamical variables, which are either even or odd simultaneously under both symmetries, must vanish. In addition, every multilinear combination of the dynamical variables is either even or odd under

both symmetries simultaneously. Therefore, r has no mode-coupling corrections. In the sense of Eq. (4.10), we can write

$$(1 - P_L)\gamma_{\vec{k}} = \gamma_{\vec{k}}. \quad (4.11)$$

Notice that this result would not change if we add other conserved dynamical variables besides $n_{\vec{k}}^{\alpha}$ and $\vec{g}_{\vec{k}}$. In the context of the mode-coupling theory it is exact to all orders. From Eq. (4.8) we can thus conclude that the quantity $r\chi_{\vec{k}}^{-1}$, which for $\vec{k} \rightarrow 0$ is proportional to $r(\partial A/\partial \xi)_{P,T}$, has no mode-coupling corrections.

C. The diffusion constant D

The evaluation of this quantity follows the ideas that were developed for the nonreactive case.⁶⁻⁸

$$D(\vec{q}) = D^0(\vec{q}) + \frac{k_B T}{\rho(2\pi)^2} \int_0^\infty dk k^2 \int_0^\pi d\theta \sin^3 \theta \frac{\chi_{\vec{q}, \vec{k}}}{\chi_{\vec{k}} k^2 \eta(\vec{k}) + (\vec{k} - \vec{q})^2 D(\vec{k} - \vec{q}) + r\chi_{\vec{k}-\vec{q}}^{-1}}. \quad (4.14)$$

In deriving Eq. (4.14) use has been made of the fact that \vec{q} parallels \hat{z} , and of the linear forms of the time-correlation function:

$$\int dt \langle n_{\vec{k}}^{\alpha}(t) n_{-\vec{k}}^{\alpha} \rangle = \frac{\chi_{\vec{k}}}{k^2 D(\vec{k}) + \tau_{T,P}^{-1}}, \quad (4.15)$$

$$\int dt \langle g_{\vec{k}}^{\alpha}(t) g_{-\vec{k}}^{\alpha} \rangle = \frac{\langle g_{\vec{k}}^{\alpha} g_{-\vec{k}}^{\alpha} \rangle (1 - \hat{e}_k \cdot \hat{e}_k)}{k^2 \eta(\vec{k})}, \quad (4.16)$$

where \hat{e}_k is a unit vector parallel to \vec{k} . In addition, the standard approximation^{6,7} of four-point-correlation functions by a product of two two-point-

$$\eta(\vec{q}) = \eta^0(\vec{q}) + \frac{k_B T}{\rho(4\pi)^2 q^2} \int_0^\infty dk k^4 \int_0^\pi d\theta \sin^3 \theta \chi_{\vec{k}} \chi_{\vec{q}, \vec{k}} \times \left(\frac{1}{\chi_{\vec{k}}} - \frac{1}{\chi_{\vec{k}-\vec{q}}} \right)^2 \frac{1}{k^2 D(k) + (\vec{q} - \vec{k})^2 D(\vec{q} - \vec{k}) + r\chi_{\vec{k}}^{-1} + r\chi_{\vec{q}-\vec{k}}^{-1}}, \quad (4.17)$$

where again the only difference with the usual result of the nonreactive case appears as the factors of $r\chi_{\vec{k}}^{-1}$ in the denominator of Eq. (4.17).

E. Self-consistent calculation of D and η

In the calculation of D and η we neglect the critical index η (not to be confused with the viscosity). Thus we assume the Ornstein-Zernike form for the susceptibility $\chi_k \approx (k^2 + \xi^2)^{-1}$. This approximation does not affect the qualitative conclusion of the analysis, but it simplifies the algebra enormously.

The calculation of $\Delta D \equiv D(k) - D^0(k)$ is presented in the Appendix. The final result is

Firstly, one realizes that $g_{\vec{k}}^{\alpha}$ can be written as a bilinear quantity. This stems from the fact that $n^{\alpha}(\vec{r})\vec{g}(\vec{r})$ equals $n(\vec{r})g^{\alpha}(\vec{r})$ where $n(r) = \sum_{i=1}^N \delta(\vec{r} - \vec{r}_i)$. Equivalently,

$$\vec{g}^{\alpha}(\vec{r}) = n^{\alpha}(\vec{r})\vec{g}(\vec{r})/n(\vec{r}). \quad (4.12)$$

Working to bilinear order, Eq. (4.12) can be rewritten as

$$\vec{g}^{\alpha}(r) = \frac{n^{\alpha}(r)\vec{g}(\vec{r})}{\langle n \rangle} \left(1 - \frac{\delta n(r)}{\langle n \rangle} + \dots \right). \quad (4.13)$$

Since we ignore the density here, we approximate $\vec{g}^{\alpha}(\vec{r})$ by the first term in Eq. (4.13); thus $g_{\vec{k}}^{\alpha}$ is itself a bilinear quantity. Using this result in (4.10) and then in (4.6), one gets a modified form of the familiar mode-coupling result for D :

correlation functions has been made. We generalized $\tau_{T,P}^{-1}$ to $r\chi_{\vec{k}}^{-1}$ in the spirit of the previous subsection. $D^0(\vec{q})$ in Eq. (4.14) is the microscopic or "bare" contribution to $D(\vec{q})$. The only difference with previous calculations is the appearance of $r\chi_{\vec{k}}^{-1}$ in the denominator of Eq. (4.14). We shall see that this modification is significant.

D. The viscosity η

The calculation of this quantity again follows the usual arguments and we therefore omit all details. The final result is

$$\Delta D = \frac{k_B T \kappa}{\rho 6\pi \eta X^2} \left(K(X) - \beta \frac{X^3}{y^3} K(y) \right), \quad (4.18)$$

where

$$\kappa \equiv \xi^{-1}, \quad X \equiv k\xi, \quad \beta \equiv \nu/(1 + \nu),$$

$$\nu \equiv r/\eta, \quad y \equiv [\nu/(1 + \nu + X)]^{1/2} X.$$

The function $K(x)$ is

$$K(x) = \frac{3}{4} [(1 + x^2) + (x^3 - x^{-1}) \tan^{-1} x].$$

One can see that if η diverges, then $\nu \rightarrow 0$ and, respectively, $\beta \rightarrow 0$ and then one gets the usual result^{6-8,18} for ΔD in a system without a chemical reaction. However, the calculation of η in the Appendix shows that η does not diverge in this

case and therefore Eq. (4.18) is a novel result that shows the influence of the chemical reaction on the diffusion constant.

Two limits of Eq. (4.18) are easily calculated:

(a) For $q \ll \kappa$ $K(X) \rightarrow X^2$, $K(y) \rightarrow y^2$, then

$$\Delta D \sim \frac{k_B T \kappa}{6\pi\eta\rho} (1 - \beta^{1/2}). \quad (4.19)$$

One sees that the usual result, i.e., that the product $\Delta D\eta$ vanishes like ξ^{-1} , is recaptured. However, the coefficient is renormalized. Remembering that $D = \alpha(\partial A/\partial \xi)_{P,T}$, we conclude that since η is not diverging in this case (cf. Appendix), α diverges like ξ .

(b) $q \gg \kappa$ $K(X) \rightarrow \frac{3}{8}\pi X^2$, $K(y) \rightarrow \frac{3}{8}\pi y^2$. Now

$$\Delta D \sim \frac{k_B T}{16(\eta+r)\rho} q. \quad (4.20)$$

Again, this result is similar to the case of a nonreactive binary mixture, except for the renormalization of the coefficient of q .

The limiting forms (4.19) and (4.20) are used in the Appendix to show that η indeed not diverge. It is shown there that the most dangerous contribution to $\Delta\eta$ is an integral of the form

$$\Delta\eta \sim \int_{\kappa}^{\kappa_c} \frac{dk k^2}{(k^3 + r k^2)}. \quad (4.21)$$

The lower limit of the integral vanishes at the critical point ($\kappa \equiv \xi^{-1}$). When there is no reaction (i.e., $r=0$) this integral diverges logarithmically and $\Delta\eta \sim \ln \xi$. (In fact, it is known that a more careful calculation of $\Delta\eta$ leads to a weak-power-law divergence rather than a logarithmic divergence.^{8,19}) However, when $r \neq 0$ the integral is protected and does not diverge. Notice that if r is extremely small (i.e., extremely slow reaction) then η would grow as $\kappa \rightarrow 0$, but its growth would be terminated once $\kappa^3 \sim r\kappa^2$. For a reasonably fast reaction, Eq. (4.21) predicts the elimination of the divergence of η .

V. DISCUSSION

Let us begin by summarizing the novel findings with regards to the dynamic critical phenomena in reactive mixtures, as the critical point is approached:

(a) A chemical reaction which occurs in a multi-component fluid is expected to slow down if all the components, or all but one, participate in the same reaction.

(b) When all the components participate in the reaction, it is expected to slow down like $[(T - T_c)/T_c]^\gamma$. When one component is nonreactive, the rate should slow down like $[(T - T_c)/T_c]^\alpha$. When two or more species do not react, we expect no slowing down of the reaction. A special situation can be the case where the reactive or

the nonreactive components are very dilute. In such a case it is possible that the reaction time would diverge more strongly. As far as binary reactive mixtures are concerned, we have found:

(c) The viscosity remains finite as $T \rightarrow T_c$.

(d) The diffusion constant vanishes like ξ^{-1} . This result might be modified slightly if the small critical exponent η is taken into account.

The results (c) and (d) are based on a mode-coupling calculation. The same calculation shows that the microscopic part of the chemical rate, r , is not affected by the reversible nonlinearities.

An important point to be stressed here is that the "slowing down of the chemical reaction" does not imply that forward or backward reactions are slowed down. It is the measured rate, which is the net difference between the forward and backward reactions, which is affected by the criticality. In fact, the condition $(\partial A/\partial \xi)_{P,T} = 0$ means that the system becomes indifferent to changes in the species concentration. In equilibrium, when $A = 0$, the reaction is balanced and the measured rate is zero. Usually, a change of ξ from ξ_{eq} builds up an affinity which acts as a driving force to restore the equilibrium. When $(\partial A/\partial \xi)_{P,T} = (\partial^2 A/\partial \xi^2)_{P,T} = 0$, a change in ξ does not create a restoring force (i.e., affinity) and the reaction continues to be balanced although $\xi \neq \xi_{eq}$. The net rate continues to be zero.

Evidently, there is a limit to the size of the disturbance which lends itself to the above analysis. In the limit where only reactants exist, say, the measured rate is not proportional to the affinity at all. In the reaction $B_2 \rightleftharpoons 2B$, say, if the concentration of B is zero, the rate is simply $k_{forward} C_{B_2}$, where C_{B_2} is the concentration of B_2 . Thus in any relaxation experiment near the critical point one might see two regions: a rapid decay into the "scaling region" and then a slow decay according to the analysis presented above. In fact, in Fig. 5 of Ref. 3(b), one can see these two regions in the recombination kinetics of $2Cl \rightleftharpoons Cl_2$.

Consequently, an experimental investigation of the phenomena discussed above might best be conducted in an unperturbed system. Noise experiments (like electrical noise, best measurable in systems with charged species like metal-ammonia solutions) or sound attenuation experiments might be ideally suitable. A theoretical discussion of these possibilities will be given later.

APPENDIX: THE CALCULATION OF $\Delta D(q)$ AND $\Delta\eta(q)$

Firstly, we notice that in Eq. (4.14) the terms containing D in the denominator can be safely neglected. Adopting the Ornstein-Zernike form for χ_k and denoting $\kappa \equiv \xi^{-1}$, we write

$$\Delta D = \frac{k_B T}{\rho(2\pi)^2} (q^2 + \kappa^2) \int_0^\pi d\theta \sin^3\theta \int_0^\infty \frac{k^2 dk}{(q^2 - 2qk \cos\theta + k^2 + \kappa^2)[k^2\eta + r(q^2 - 2qk \cos\theta + k^2 + \kappa^2)]}. \quad (\text{A1})$$

Using the change of variables $t = \cos\theta$, $X = q\xi$, $\nu = r/\eta$, we get

$$\Delta D = \frac{k_B T \kappa (X^2 + 1)}{\rho(2\pi)^2 \eta} \int_{-1}^1 dt (1 - t^2) \int_0^\infty \frac{k^2 dk}{(X^2 - 2Xkt + k^2 + 1)[k^2 + \nu(X^2 - 2Xkt + k^2 + 1)]}, \quad (\text{A2})$$

where the quantity $k\xi$ is again denoted as k .

We notice that the boundaries of the integral can be changed to 0 to 1 in the t integral and $-\infty$ to ∞ in the k integral. Denoting $\beta \equiv \nu/(1 + \nu)$ we get

$$\Delta D = \frac{k_B T \kappa (1 + X^2)}{\rho(2\pi)^2 \eta (1 + \nu)} \int_0^1 dt (1 - t^2) \int_{-\infty}^\infty \frac{k^2 dk}{(k^2 - 2Xtk + X^2 + 1)[k^2 + \beta(-2Xtk + X^2 + 1)]}. \quad (\text{A3})$$

This result is broken up into two integrals:

$$\Delta D = \frac{k_B T \kappa (1 + X^2)}{\rho(2\pi)^2 \eta} \left(\int_0^1 dt (1 - t^2) \int_{-\infty}^\infty \frac{dk}{k^2 - 2Xtk + X^2 + 1} - \beta \int_0^1 dt (1 - t^2) \int_{-\infty}^\infty \frac{dk}{k^2 - 2Xt\beta k + \beta X^2 + \beta} \right). \quad (\text{A4})$$

We now use the integrals

$$\int_{-\infty}^\infty \frac{dk}{k^2 + \beta(-2Xtk + 1 + X^2)} = \frac{\pi}{\beta^{1/2}[1 + X^2(1 - \beta t^2)]^{1/2}} \quad (\text{A5})$$

and

$$\int_0^1 dt \frac{1 - t^2}{1 - \frac{X^2}{1 + X^2} t^2} = \frac{(1 + X^2)^{1/2}}{2} [X^{-2} + (X^{-1} - X^{-3}) \tan^{-1} X], \quad (\text{A6})$$

to arrive at the final form

$$\Delta D = \frac{k_B T \kappa}{\rho 6\pi \eta X^2} \left(K(X) - \beta \frac{X^3}{Y^3} K(Y) \right), \quad (\text{A7})$$

where

$$K(X) = \frac{3}{4} [(1 + X^2) + X^3 - X^{-1}] \tan^{-1} X, \quad (\text{A8})$$

$$Y \equiv \left(\frac{\nu}{1 + \nu + X} \right)^{1/2} X. \quad (\text{A9})$$

The limiting forms of $\Delta D(q)$ for large and small q are given in Eqs. (4.19) and (4.20).

We show now that $\Delta\eta(q)$ does not diverge. It is sufficient to consider the limit $q \rightarrow 0$ of Eq. (4.17), since this limit reveals the most divergent part, if it exists. Thus,

$$\Delta\eta(q \rightarrow 0) = \frac{k_B T}{8\pi^2 \rho} \int_0^\pi d\theta \sin^3\theta \cos^2\theta \int_0^\infty \frac{dk k^6}{(k^2 + \kappa^2)^2 [k^2 D(k) + r(k^2 + \kappa^2)]} \quad (\text{A10})$$

where again the Ornstein-Zernike form has been used. The θ integration is trivial, and performing it we get

$$\Delta\eta = \frac{k_B T}{30\pi^2} \int_0^{k_c} \frac{dk k^6}{(k^2 + \kappa^2)^2 [k^2 D(k) + r(k^2 + \kappa^2)]}. \quad (\text{A11})$$

The cutoff k_c is introduced as usual to eliminate spurious (noncritical) divergencies. The integral is separated into two parts:

$$\int_0^{k_c} = \int_0^\kappa + \int_\kappa^{k_c}.$$

In the first integral we use the limiting form $k^2 D(k) \sim \kappa k^2$ and see that it vanishes like κ when $\kappa \rightarrow 0$. In the second integral we use $k^2 D(k) \sim k^3$ to find

$$\Delta\eta \sim \int_\kappa^{k_c} \frac{dk k^2}{(k^3 + r k^2)}. \quad (\text{A12})$$

The dangerous limit is the lower one, $k \sim \kappa$, but when $\kappa \rightarrow 0$ this integral is now bounded in the lower limit and does not diverge. We can thus conclude that the existence of the chemical reaction removed the divergence of η .

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