Nonlinear behavior at a chemical instability: A detailed renormalization-group analysis of a case model

Isaac Goldhirsch and Itamar Procaccia
Chemical Physics Department, Weizmann Institute of Science, Rehovot, Israel
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A theory that is suitable for the analysis of the nonlinear behavior at or very near to a far-from-equilibrium instability point is presented. The theory is based on the idea that far-from-equilibrium instabilities, like equilibrium critical systems, have a critical space dimensionality, d_c, above which a quasilinear treatment yields the correct values of the critical exponents. The results for physical systems (i.e., space dimensionality $d \leq 3$) are obtained by an ϵ expansion, in a manner analogous to the one used in the dynamical renormalization group. We treat in detail a case model of a chemical instability. The main result is that the critical exponents differ from those predicted by the quasilinear approximation or by master equations (i.e., the so-called "classical" exponents). We show that great care must be taken with the correlation of random forces, since a faulty choice of this correlation can yield results that differ significantly from those obtained by using the correct correlation.

I. INTRODUCTION

Instabilities and transition phenomena in systems far from equilibrium have been a subject of rapidly growing interest in recent years.[1] Much stress has been put on the analogy of these phenomena to equilibrium phase transition and criticality. It has been pointed out that enhancement of fluctuations, long-range order, and critical slowing down are typical to nonequilibrium transition phenomena in much the same way as they characterize equilibrium critical points.[2]

Surprisingly, the consequences of this enhancement of fluctuations and long-range correlations were not fully accounted for in theoretical treatments of nonequilibrium instabilities. The most obvious of these consequences is that the central limit theorem, which provides justification for solutions of master equations and for quasilinear approximations,[3,4] no longer hold near a bifurcation or an instability point.[3] A full treatment of the effects of nonlinearities is needed.

The purpose of this paper is to suggest a method which is suitable for the analysis of fluctuations and the effects of nonlinearities very near to an instability point.

The method is based on the idea of critical dimensionality. As has been pointed out by Mori,[3] the spatial dimensionality provides an important parameter for specifying the stochastic properties of nonequilibrium fluctuation in much the same way as it does for equilibrium critical points. There is a critical dimensionality d_c above which the fluctuations are small even at close proximity to an instability, and a quasilinear approximation provides an exact solution to many aspects of the problem in the thermodynamic limit. The question that remains is how to assess the behavior at physical dimensionalities. To this aim we adapt in this paper the techniques of the dynamic renormalization group[5] to provide an ϵ expansion which yields results for $d = d_c - \epsilon$. The main result of this paper is that we find the critical exponents at an instability to differ from their so-called "classical" value which is obtained from the quasilinear approximation (see below). In addition the effects of nonlinearities on line shapes can be found.

We chose to present here a detailed analysis of a simple example of a chemical instability. The main problem in adapting renormalization-group techniques to this example is that the fluctuation-dissipation theorem does not exist in its equilibrium form and one has to consider explicitly the renormalization of the random force. It will be argued that a faulty choice of random force might result in serious changes in critical behavior and even in the disappearance of criticality.

The structure of the paper is as follows: in Sec. II we present the model, discuss it in the quasilinear approximation, and review Mori's scaling method to determine d_c. In Sec. III we lay out the ϵ expansion and discuss in detail the renormalization group. In Sec. IV we solve for the fixed point and for the critical exponents. In Sec. V we show how criticality is removed by a change in the random force correlation function. Section VI offers conclusions and a discussion.

II. THE MODEL

For simplicity we chose a model which is very well known and has been treated many times in the literature. This is the Schlögl model for a chemical instability[6]

$$\begin{aligned} A + X &\underset{k_2}{\overset{k_1}{\rightleftharpoons}} 2X\,, \\ M + X &\underset{k_4}{\overset{k_3}{\rightleftharpoons}} N\,. \end{aligned} \tag{2.1}$$

The macroscopic rate equations for the concentration of X, denoted by $\rho(r,t)$, is

$$\frac{\partial\rho(r,t)}{\partial t}=D\nabla^2\rho(r,t)+B+a\rho(r,t)-C\rho^2(r,t) . \quad (2.2)$$

Here we assume that the concentrations of A, M, and N are kept constant and $B=k_4[N]$, $a=k_1[A]-k_3[M]$, and $C=k_2$.

The steady-state solution of Eq. (2.2) is

$$\rho^{ss}=\frac{a+\gamma}{2c}, \quad (2.3a)$$

$$\gamma=(a^2+4CB)^{1/2} . \quad (2.3b)$$

When $B=0$ one finds a transition point $a=0$ for which ρ^{ss} changes from 0 ($a<0$) to $\rho^{ss}=(a/c)$ ($a>0$). We shall be interested in the behavior near this point. In all our analyses we confine ourselves to approaching the critical point from above.

A. Stochastic description

The stochasticity and the spatial dimensionality are introduced when one realizes that Eq. (2.2) is only an averaged description of the slowly varying local densities in the system.

The density which appears in the equation of motion, denoted by $A(r,t)$, is in fact

$$A(r,t)=\int_{k\Lambda}\frac{d^dk}{2\pi}\int\frac{d\omega}{2\pi}A(\vec{k},\omega)e^{i\vec{k}\cdot\vec{r}-i\omega t} , \quad (2.4)$$

where Λ is an upper cutoff on the $|\vec{k}|$'s. The equation of motion for $A(r,t)$ can be generally written as

$$\frac{\partial A(r,t)}{\partial t}=-h(A)+R(r,t) , \quad (2.5)$$

where $R(t)$ is the random force that is generated by the elimination of rapidly varying degrees of freedom. As is commonly assumed,

$$\langle R(r,t)\rangle=0 ,$$
$$\langle R(r,t)R(r',t')\rangle=2E(r,r')\delta(t-t') . \quad (2.6)$$

The density $A(r,t)$ can be decomposed exactly into a systematic part and fluctuating parts. Following Mori[3] we define

$$A(r,t)\equiv y(r,t)+Z(r,t) , \quad (2.7)$$

$$\frac{\partial y(r,t)}{\partial t}=-h(y) , \quad (2.8)$$

$$\frac{\partial Z}{\partial t}=-[h(y+Z)-h(y)]+R(r,t) . \quad (2.9)$$

Clearly, Eqs. (2.7)–(2.9) are exactly equivalent to (2.5).

For the case treated here Eqs. (2.8) and (2.9) assume the form

$$\frac{\partial y(r,t)}{\partial t}=D\nabla^2y(r,t)+B+ay(r,t)-Cy^2(r,t) , \quad (2.10a)$$

$$\frac{\partial Z(r,t)}{\partial t}=D\nabla^2Z(r,t)+aZ(r,t)-2Cy(r,t)Z(r,t)-CZ^2(r,t)+R(r,t) . \quad (2.10b)$$

Equation (2.10a) is identical in structure to Eq. (2.2). Its steady-state solution is $y_{ss}=(a+\gamma)/2C$, similar to Eq. (2.3a). Since we are interested in the properties of the system in the steady state we substitute this value of y in Eq. (2.10b). The resulting equation is

$$\frac{\partial Z(r,t)}{\partial t}=D\nabla^2Z(r,t)-\gamma Z(r,t)-CZ^2(r,t)+R(r,t) \quad (2.11)$$

when the system is in the steady state, the correlation of the random force reads[4]

$$E(r,r')=\tfrac{1}{2}\{B+(k_1[M]+k_2[A])y_{ss}+Cy_{ss}^2\}\delta(r-r')+D\nabla_r\cdot\nabla_{r'}[y_{ss}\delta(r-r')] . \quad (2.12)$$

Notice that the four parameters a, B, C, and D which characterize Eqs. (2.10) are replaced by the four parameters γ, B, C, and D in Eqs. (2.11) and (2.12). Equation (2.3b) furnishes a relation between these sets of parameters. As seen from the deterministic analysis, there is criticality when $B=0$ but not otherwise. We shall show that the renormalization-group (RG) analysis is consistent with this result.

B. Quasilinear approximation

In the quasilinear approximation the critical exponents can be found on the basis of dimensional considerations alone. Writing the linearized equations as

$$\frac{dy_{\vec{k}}(t)}{\partial t}=-Dk^2y_{\vec{k}}(t)-\gamma y_{\vec{k}}(t) , \quad (2.13)$$

where $y_{\vec{k}}(t)$ is the Fourier component of $y(r,t)-y_{ss}$, we see immediately that there is only one length scale in the problem,

$$\xi=(D/\gamma)^{1/2} \quad (2.14)$$

which diverges like $\gamma^{-1/2}$ as the bifurcation is approached from below or from above. Similarly one can conclude that the amplitude of the fluctuations diverges like γ^{-1}. Evidently, the quasilinear approximation predicts its own failure as the instability is approached. Our main task is to determine how the critical exponents are modified by the nonlinearities which must be considered since the fluctuations grow and linearization is not allowed.

C. Scaling and critical dimensionality

At equilibrium the central limit theorem states that

$$\frac{Z(r,t)}{y(r,t)} \propto \frac{1}{\sqrt{V}} \tag{2.15}$$

and fluctuations are always relatively small when the thermodynamic limit is taken. This property is lost near criticality. It was suggested by Mori that Z and y should be scaled differently. Denoting the scaling parameter by b, we define the scaling exponents α, τ, β, θ and ψ by

$$y(r,t) = b^{-\alpha}\tilde{y}(r/b, t/b^{\theta}), \tag{2.16}$$

$$Z(r,t) = b^{-\beta}\tilde{Z}(r/b, t/b^{\theta}), \tag{2.17}$$

and

$$R(r,t) = b^{-(d+\psi+\theta)/2}\tilde{R}(r/b, t/b^{\theta}). \tag{2.18}$$

Here d is the space dimensionality and $\tilde{y}$, $\tilde{Z}$, and $\tilde{R}$ are scale invariants at criticality. In principle the scaling exponents are b dependent but we shall be interested only in their asymptotic ($b \to \infty$) values. The crux of the method lies in the fact that α and β might be d dependent. There might be a d_c for which $\alpha > \beta$ if $d < d_c$ and $\alpha < \beta$ for $d > d_c$, even at criticality. If this is the case, then for $d > d_c$ the fluctuating part $Z(r,t)$ is small compared to $y(r,t)$ when $b \to \infty$ and a linearization procedure is justified and allows for an exact solution of the problem (in the thermodynamic limit).

We can find d_c and the scaling exponents for $d > d_c$ by *assuming* that there exists a d_c and then checking the consistency of this assumption.

Using Eq. (2.14) above d_c we see that $\gamma \propto b^{-2}$. Consequently, from Eq. (2.3), $\alpha = 2$ when $B = 0$. The other exponents are found from Eqs. (2.12) and (2.13). We rewrite Eq. (2.12) in terms of scale invariants that are denoted by a tilde

$$b^{-\beta-\theta}\frac{\partial \tilde{Z}}{\partial \tilde{t}} = Db^{-\beta-2}\tilde{\nabla}^2\tilde{Z} - b^{-2}b^{-\beta}\tilde{\gamma}\tilde{Z} - Cb^{-2\beta}\tilde{Z}^2 + b^{-(d+\psi+\theta)/2}\tilde{R}. \tag{2.19}$$

The nonlinear term is of no consequence for $d > d_c$. Comparing the lhs to either the first or second term on the rhs we find $\theta = 2$. From the last term on the rhs we get

$$\beta = (d + \psi - \theta)/2. \tag{2.20}$$

An additional relation is obtained from Eqs. (2.7) and (2.12). When $B = 0$, the second term in the curly brackets has the smallest exponent, and it scales like $b^{-\theta-d-2}$ which with Eq. (2.7) means that

$$-(d + \psi + \theta) = -(\theta + d + 2). \tag{2.21}$$

Together with (2.20) we find

$$\psi = 2, \quad \beta = \tfrac{1}{2}d. \tag{2.22}$$

Consequently, $\beta > \alpha$ if $d > 4$, determining d_c to be 4. As a consistency check we note that the nonlinear term in Eq. (2.19) is indeed irrelevant for $d > 4$, $b \to \infty$ and is relevant for $d < 4$.

These results are incorrect for $d < 4$. Since the nonlinearity becomes important for $d < 4$, we must consider now a method that takes it into account.

III. ϵ expansion

A. Diagrammatic expansion

The basis of our analysis is Eq. (2.11). Defining the Fourier components $Z_{\vec{k}\omega}$ by

$$Z(r,t) = \int_{k<\Lambda} \frac{d^d k}{(2\pi)^d} \int \frac{d\omega}{2\pi} Z_{\vec{k}\omega} e^{i\vec{k}\cdot\vec{r} - i\omega t} \tag{3.1}$$

We rewrite Eq. (2.12) in $\vec{k}$, ω space:

$$(-i\omega t + Dk^2 + \gamma)Z_{\vec{k}\omega} = -C\int_{q<\Lambda} \frac{d^d q}{(2\pi)^d}\int \frac{d\nu}{2\pi} Z_{\vec{k}-\vec{q},\omega-\nu} Z_{\vec{q},\nu} + R_{\vec{k}\omega}, \tag{3.2}$$

where $R_{\vec{k}\omega}$ is defined similarly to $Z_{\vec{k}\omega}$.

Defining the un-normalized propagator $G^0(\vec{k},\omega)$ by

$$G^0(\vec{k},\omega) = (-i\omega + Dk^2 + \gamma)^{-1} \tag{3.3}$$

we have

$$Z_{\vec{k}\omega} = G^0(\vec{k},\omega)R_{\vec{k}\omega} - G^0(\vec{k},\omega)C\int_{q<\Lambda} \frac{d^d q}{(2\pi)^d}\int \frac{d\nu}{2\pi} Z_{\vec{k}-\vec{q},\omega-\nu} Z_{\vec{q},\nu}. \tag{3.4}$$

We wish to extract the asymptotic behavior (small k, small ω) near the bifurcation point. To this aim we adapt the procedure of the renormalization group.[5,7] Thus we wish to eliminate progressively modes with $\Lambda/b < k < \Lambda$. This is done by formally solving the equation for $Z_{\vec{k}\omega}$ with $k > \Lambda/b$ as a power series in C. These formal solutions are substitued in the equation for $Z_{\vec{k}\omega}$ with $k < \Lambda/b$ to eliminate its explicit coupling to the high-k components. Finally we average over the part of the random force that acts in the shell $\Lambda/b < k < \Lambda$. After each such elimination we change the scale of $Z_{\vec{k}\omega}$ and of k and ω and rewrite the resulting equation in the form of Eq. (3.4). The parameters D, γ, C as well as ω and $R_{\vec{k}\omega}$ will be renormalized. The recursion relations of these quantities and their fixed point will yield the needed information.

Since, as we show in the following, the fixed point value of C is of the order $\epsilon \equiv d_c - d$, we assume that we start with a C that is already in the vicinity of the fixed point (as is usually done in RG analyses). Consequently C can be regarded as a small parameter.

We write Eq. (3.4) diagrammatically as in Fig. 1(a). The $Z_{\vec{k}\omega}$ legs with a slash denote modes with $k > \Lambda/b$ that have to be eliminated. Since eventually we average over the random force, only diagrams with even number $R_{\vec{k}\omega}$ in them survive. To order C^2 the diagrams that contribute to the iteration are shown in Fig. 1(b). The third diagram on the rhs disappears upon averaging. The reason is that k is conserved at every vertex and thus the propagator that connects the two vertices can have only $k = 0$. But it comes originally from a high-k component, and this is impossible. The fourth diagram also disappears upon averaging but it must be considered since it renormalizes $R_{\vec{k}\omega}$, (which indeed vanishes upon averaging) and its correlation function $\langle R_{\vec{k}\omega} R_{\vec{k}'\omega'}\rangle$. The final equations are exhibited in Figs. 1(c) and 1(d).

B. Intermediate parameters

The evaluation of the diagrams is straightforward. Writing

$$\langle R_{\vec{k}\omega} R_{\vec{k}'\omega'}\rangle = T\delta(\vec{k}+\vec{k}')\delta(\omega+\omega') \tag{3.5}$$

we find that the diagram in Fig. 1(c) is

$$4C^2 T G^0(\vec{k},\omega) I_{\vec{k}\omega} Z_{\vec{k}\omega}\,,$$

where

$$I_{\vec{k}\omega} = \int_{\Lambda/b}^{\Lambda} \frac{d^d q}{(2\pi)^d} \int \frac{d\omega'}{2\pi} \,|G^0(\vec{q},\omega')|^2 G^0_{\vec{k}-\vec{q},\,\omega-\omega'}\,. \tag{3.6}$$

We choose the differential renormalization-group procedure in which $b = 1 + \delta$, where δ is small.[8] In Appendix A we outline the calculation which yields the expression for this diagram, denoted by $\delta G^0(\vec{k},\omega) M Z_{\vec{k}\omega}$, where

$$M = \frac{4c^2 T}{(2\pi)^{d+1}} \left[\frac{\pi}{2} K_d \frac{\Lambda^d}{(D\Lambda^2+\gamma)^2} + k^2 D\pi K_d \times \left(\tfrac{1}{6} D \frac{\Lambda^{d+2}}{(D\Lambda^2+\gamma)^4} - \frac{1}{4}\frac{\Lambda^d}{(D\Lambda^2+\gamma)^3} \right) + i\omega \frac{\pi}{4} K_d \frac{\Lambda^d}{(D\Lambda^2+\gamma)^3} \right]. \tag{3.7}$$

The equation of Fig. 1(c) can now be written in the form

$$[1 - \delta G^0(\vec{k},\omega) M] Z_{\vec{k}\omega} = G^0(\vec{k},\omega) R^I_{\vec{k}\omega} - G^0(\vec{k},\omega) C \int_{q<\Lambda/b} \frac{d^d q}{(2\pi)^d} \times \int \frac{d\nu}{2\pi} Z_{\vec{k}-\vec{q},\,\omega-\nu} Z_{\vec{q},\nu}\,, \tag{3.8}$$

where $R^I_{\vec{k}\omega}$ is the intermediate form of $R_{\vec{k}\omega}$ which is yet to be found. Alternatively, we have

$$Z_{\vec{k}\omega} = \frac{1}{G^0(\vec{k},\omega) - \delta M} R^I_{\vec{k}\omega} - \frac{C}{G^0(\vec{k},\omega) - \delta M} \times \int_{q<\Lambda/b} \frac{d^d q}{(2\pi)^d} \int \frac{d\nu}{2\pi} Z_{\vec{k}-\vec{q},\,\omega-\nu} Z_{\vec{q},\nu}\,. \tag{3.9}$$

The new propagator $G^I(\vec{k},\omega)$ is defined as $G^0 - \delta M$ and is written as

$$G^I(\vec{k},\omega) = (-i\omega\Omega^I + k^2 D^I + \gamma^I)^{-1}\,, \tag{3.10}$$

where

$$D^I = D - \delta 4FD\left(\tfrac{1}{6} D \frac{\Lambda^2}{D\Lambda^2+\gamma} - \frac{1}{4}\right), \tag{3.11}$$

$$\Omega^I = 1 + \delta F\,, \tag{3.12}$$

$$\gamma^I = \gamma - \delta 2F(D\Lambda^2+\gamma)\,, \tag{3.13}$$

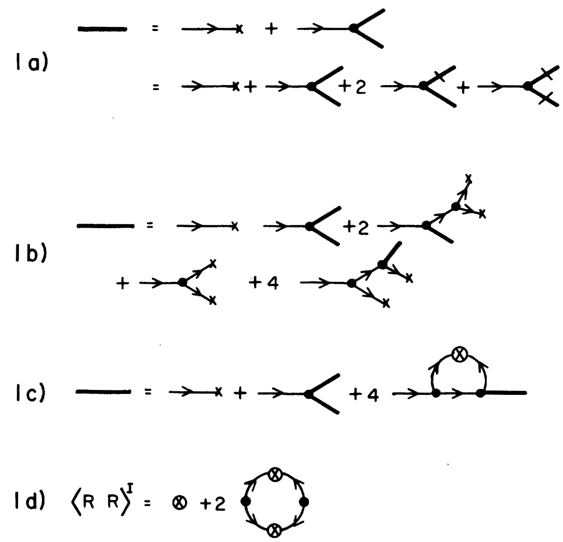

FIG. 1. Diagrammatic description of the renormalization-group procedure. A heavy line denotes $Z_{\vec{k}\omega}$. A light line with an arrow denotes $G^0_{\vec{k}\omega}$. The random force is denoted by X. A heavy dot stands for $-C\int_{q<\Lambda}[d^dq/(2\pi)^d]\int d\nu/2\pi$. An X in a circle denotes $\langle R_{\vec{k}\omega}R_{\vec{k}'\omega'}\rangle$. Part (a) is Eq. (3.4). In the second line the contributions of high k's are denoted by a slash. (b) represents all the diagrams that contribute to $O(C^2)$ and that have an even number of $R_{\vec{k}\omega}$. (c) shows the diagrams that survive an averaging over the random force which acts in the shell $\Lambda/b < k < \Lambda$. (d) shows the diagram that renormalizes the random-force correlation function. The diagram stems from the first diagram on the second line of part (b).

where

$$F=C^2T\frac{\pi}{(2\pi)^{d+1}}K_d\frac{\Lambda^d}{(D\Lambda^2+\gamma)^3}. \quad (3.14)$$

Notice that to this order we have no renormalization of the vertex and thus we add the equation

$$C^I=C. \quad (3.15)$$

The diagram in Fig. 1(d) can be computed along the same lines, yielding the intermediate form of the $\langle RR\rangle$ correlation function. The result is

$$T^I=T+\delta FT. \quad (3.16)$$

C. Rescaling and renormalization

The last step in the implementation of the renormalization-group procedure is rescaling, which yields the renormalized form of the relevant quantities. To this aim we introduce the quantity $\tilde{Z}_{b\vec{k},b^\theta\omega}$ defined by

$$Z_{\vec{k}\omega}=b^{-\beta+d+\theta}\tilde{Z}_{b\vec{k},b^\theta\omega}. \quad (3.17)$$

The difference between Eqs. (3.17) and (2.17) is due to Eq. (3.1). In addition, we use the fact that $b=1+\delta$ to write Eq. (3.12) in the form

$$\Omega^I=b^F. \quad (3.18)$$

In (3.18) and subsequently the exponentiation is correct to $O(\delta)$.

We rewrite now Eq. (3.9) and (3.10) in terms of scaled quantities

$$b^{-\beta+d+\theta}\tilde{Z}_{b\vec{k},b^\theta\omega}=\frac{R^I_{\vec{k}\omega}}{-i(\omega b^\theta)b^{F-\theta}+b^{-2}D^I(bk)^2+\gamma^I}-\frac{b^{-2\beta+d+\theta}}{-i(\omega b^\theta)b^{F-\theta}+b^{-2}D^I(bk)^2+\gamma^I}\times\int_{q<\Lambda/b}\frac{d^d(qb)}{(2\pi)^d}\int\frac{d(\nu b^\theta)}{2\pi}\tilde{Z}_{b(\vec{k}-\vec{q}),b^\theta(\omega-\nu)}Z_{b\vec{q},b^\theta\nu}. \quad (3.19)$$

Notice that $R^I_{\vec{k},\omega}$ is not yet written in terms of scaled quantities. Multiplying numerators and denominators on the rhs by $b^{\theta-F}$ and the equation by $b^{\beta-d-\theta}$ we find the equation ($\tilde{k}\equiv b\vec{k}$, $\tilde{\omega}\equiv b^\theta\omega$)

$$\tilde{Z}_{\tilde{k}\tilde{\omega}}=\frac{b^{\beta-F-d}R^I_{\vec{k}\omega}}{-i\tilde{\omega}+b^{\theta-F-2}D^I\tilde{k}^2+b^{\theta-F}\gamma^I}-\frac{Cb^{-\beta-F+\theta}}{-i\tilde{\omega}+b^{\theta-F-2}D^I\tilde{k}^2+b^{\theta-F}\gamma^I}\times\int_{\tilde{q}<\Lambda}\frac{d^d\tilde{q}}{(2\pi)^d}\int\frac{d\tilde{\nu}}{2\pi}\tilde{Z}_{\tilde{k}-\tilde{q},\tilde{\omega}-\tilde{\nu}}\tilde{Z}_{\tilde{q},\tilde{\nu}}. \quad (3.20)$$

Equation (3.20) is the renormalized equation if we identify

$$R^R_{\tilde{k},\tilde{\omega}}=b^{\beta-F-d}R^I_{\vec{k}\omega}. \quad (3.21)$$

This equation must be accompanied consistently with Eq. (3.16). Once Eq. (3.21) is written, the rest of the renormalized quantities are read from Eq. (3.20):

$$D^R=D^Ib^{\theta-F-2}, \quad (3.22)$$

$$\gamma^R=\gamma^Ib^{\theta-F}, \quad (3.23)$$

$$C^R=Cb^{-\beta-F+\theta}. \quad (3.24)$$

We now use Eq. (3.21) to find T^R. Writing

$$\langle R^R_{\tilde{k}\tilde{\omega}}R^R_{\tilde{k}',\tilde{\omega}'}\rangle=b^{2\beta-2F-2d}\langle R^I_{\tilde{k}\tilde{\omega}}R^I_{\tilde{k}',\tilde{\omega}'}\rangle \quad (3.25)$$

we have by definition of $R^I_{\vec{k}\omega}$

$$\langle R^R_{\tilde{k}\omega}R^R_{\tilde{k}',\omega'}\rangle=b^{2\beta-2F-2d}T^I\delta(\vec{k}+\vec{k}')\delta(\omega+\omega')=b^{2\beta-2F+\theta-d}T^I\delta(\tilde{k}+\tilde{k}')\delta(\tilde{\omega}+\tilde{\omega}'). \quad (3.26)$$

From Eq. (3.16) we have

$$T^I=b^FT \quad (3.27)$$

which means that finally

$$T^R=b^{2\beta-F+\theta-d}T. \quad (3.28)$$

To obtain a consistent RG scheme the renormalized equations of motion have to be identical in form to the original equations, with the original parameters being replaced by the renormalized ones. As we argued before, if $B\neq 0$ we expect no criticality. This will be shown to be true in Sec. V. At this point, however, we set $B=0$. The RG relevant term in the noise correlation function is $(k_1[M]+k_2[A])y_{ss}$. The other terms scale more strongly and are therefore irrelevant. Using the value of $y_{ss}=\gamma/c$ the only way to get a consistent (self-similar) RG scheme is to demand that the renormalized noise correlation function is

$$T^R=K\frac{\gamma^R}{C^R}, \quad (3.29)$$

where $K=(k_1[M]+k_2[A])$. This condition will determine β. Using Eqs. (3.13), (3.15), (3.23), and (3.20) we find

$$T^R=Tb^{\beta-2\overline{F}(D\Lambda^2)-2F}, \quad (3.30)$$

where $\overline{F}=F/\gamma$. Comparing (3.28) and (3.30) we find

$$b^\beta=b^{d-\theta-2\overline{F}D\Lambda^2-F}. \quad (3.31)$$

We see that the previous result of the linearized theory above d_c, $\beta=\frac{1}{2}d$, is not likely to be refound. At any rate Eq. (3.31) is an important equation that will yield the recursion relations.

D. Recursion relations

Substituting Eq. (3.31) in Eqs. (3.24) we get the recursion relation

$$\frac{dC}{db}=(2\theta-d+2\bar{F}D\Lambda^2)C\,. \tag{3.32}$$

This recursion relation must be consistent with the analysis of Sec. II. In other words, we hope to find that for $d>4$ $dC/db<0$ and vice versa. We will see that this is the case.

The other recursion relations are obtained from Eqs. (3.11), (3.13), (3.22), and (3.23):

$$\frac{d\gamma}{db}=(\theta-3F-2\bar{F}D\Lambda^2)\gamma\,, \tag{3.33}$$

$$\frac{dD}{db}=D(\theta-F-2)-4FD\left(\frac{1}{6}\frac{D\Lambda^2}{D\Lambda^2+\gamma}-\frac{1}{4}\right). \tag{3.34}$$

These recursion relations have a nontrivial fixed point that is obtained in the next section.

IV. FIXED POINT AND CRITICAL EXPONENTS

A. Fixed point

It is useful to rewrite the recursion relations (3.32)–(3.39) in terms of the variables $Q\equiv\gamma/D\Lambda^2$, $\bar{F}=F/\gamma$, and D. Moreover we require that $D^R=D$. Thus Eq. (3.39) becomes a constraint equation that guarantees the preservation of the form of the diffusion process. Starting with Eq. (3.34) we assume (and confirm *a posteriori* that γ is $O(\epsilon)$ where $\epsilon=d_c-d$. Thus the condition $dD/db=0$ yields

$$\theta=2+\tfrac{2}{3}\bar{F}QD\Lambda^2\,. \tag{4.1}$$

This result allows us to find d_c. Assuming (and confirming later) that $\bar{F}^*$ is $O(\epsilon)$ we see from Eq. (3.32) that $d_c=4$, indeed, consistent with Sec. III.

From Eq. (3.14) we have

$$\bar{F}=C\frac{\pi}{(2\pi)^{d+1}}K_d\frac{\Lambda^d}{(D\Lambda^2+\gamma)^3} \tag{4.2}$$

or

$$\frac{d\bar{F}}{db}=\frac{\bar{F}}{C}\frac{dc}{db}-3\frac{\bar{F}}{1+Q}\frac{dQ}{db}\,. \tag{4.3}$$

From Eq. (3.33) we have

$$\frac{dQ}{db}=(\theta-3\bar{F}QD\Lambda^2-2\bar{F}D\Lambda^2)Q\,. \tag{4.4}$$

Combining Eqs. (3.32), (3.33), (4.1), and (4.3) we find

$$\frac{d\bar{F}}{db}=(4-d)\bar{F}+(2D\Lambda^2)\bar{F}^2-6Q\bar{F}\,. \tag{4.5}$$

Using (4.1) in (4.4) we have

$$\frac{dQ}{db}=(2-2D\Lambda^2\bar{F}-\tfrac{7}{3}QD\Lambda^2\bar{F})Q\,. \tag{4.6}$$

The second and third terms in the parentheses are $O(\epsilon)$ and $O(\epsilon^2)$, respectively. Thus the only fixed point for Q is

$$Q^*=0\,. \tag{4.7}$$

From (4.5) we then find

$$\bar{F}^*=-\epsilon/2D\Lambda^2 \tag{4.8}$$

and from (4.2)

$$C^*=-\epsilon D^2\frac{(2\pi)^{d+1}}{K_d\pi} \tag{4.9}$$

to first order in ϵ.

B. Linearization and critical exponents

The most important information is obtained from the linearized recursion equations around the fixed point. We find

$$\frac{d\delta\bar{F}}{db}=-\epsilon\delta\bar{F}+\frac{3\epsilon}{D\Lambda^2}\delta Q\,, \tag{4.10}$$

$$\frac{d\delta Q}{db}=(2+\epsilon)\delta Q\,. \tag{4.11}$$

The eigenvalues are evidently $\lambda_1=2+\epsilon$ and $\lambda_2=-\epsilon$.

Defining the critical exponent of the correlation length by

$$\xi=(\delta Q)^{-\nu} \tag{4.12}$$

we find[9]

$$\nu=1/\lambda_1=\tfrac{1}{2}(1-\tfrac{1}{2}\epsilon)\,. \tag{4.13}$$

In three dimensions $\nu=\frac{1}{4}$. We recall that the linearized theory predicted $\nu=\frac{1}{2}$.

Similarly the relaxation time exponent will be denoted by x

$$\tau_k=(\delta Q)^{-x}f(k\xi)=\xi^{-x/4}f(k\xi)\,. \tag{4.14}$$

Since we found $\theta=2$ we conclude that $x=\frac{1}{2}$ compared to 1 in the linearized theory.

Most interesting is the behavior of the static correlation $\langle Z_{\vec{q}}Z_{\vec{q}}\rangle$ and the relative fluctuations $\langle Z_{\vec{q}}Z_{\vec{q}}\rangle^{1/2}/\rho$. Writing

$$\chi(\vec{q})=\frac{\langle Z_{\vec{q}}Z_{\vec{q}^1}\rangle}{\delta(\vec{q}+\vec{q}^1)}=b^{-2\beta+d}\frac{\langle\tilde{Z}_{\vec{q}}\tilde{Z}_{\vec{q}^1}\rangle}{\delta(\vec{q}+\vec{q}^1)}\,, \tag{4.15}$$

we use Eq. (3.31) to find that $\beta=2$ and

$$\chi(\vec{q})=b^{-\epsilon}\chi(\vec{b}q,\,\xi/b)\,. \tag{4.16}$$

Choosing $b=\xi$ we get

$$\chi(\vec{q})=\xi^{-\epsilon}\chi(\vec{q}\xi) \tag{4.17}$$

meaning that $\chi(q)$ vanishes at the critical point. The relative fluctuations, however, diverge since

$$\frac{\chi^{1/2}(\vec{q})}{\rho}=C\frac{\xi^{-\epsilon/2}}{\gamma}f(q\xi)=\xi^{2+\epsilon-\epsilon/2}f(q\xi)\,. \tag{4.18}$$

In three dimensions the dicergence is like $\xi^{2.5}$.

These results are in qualitative agreement with the master-equation approach,[10] where it is also found that the fluctuations vanish whereas their relative size diverges. The critical exponents, however, are different.

V. RENORMALIZATION WHEN CRITICALITY IS REMOVED

We now consider the case that the parameter B in Eq. (2.12) is not zero. The quasilinear analysis indicates that there is no criticality in this case and ξ is finite. It is important to see that the method presented in Sec. IV predicts the same thing. In fact, we shall show here that keeping track of the renormalization of the random force force is of great importance in determining the critical behavior.

First, we consider the case that the correlation function of the random force is simply a constant. Thus the requirement (3.29) becomes $T^R=T$. From Eq. (3.28) we see that the condition for that is

$$b^{2\beta-F+\theta-d}=1 \tag{5.1}$$

or

$$b^{\beta}=b^{F/2-\theta/2+d/2}\,. \tag{5.2}$$

The recursion relations now assume the following form:

$$\frac{dc}{db}=(\tfrac{3}{2}\theta-\tfrac{1}{2}d-\tfrac{3}{2}F)C\,, \tag{5.3}$$

$$\frac{d\gamma}{db}=\gamma\theta-3F\gamma-2FD\Lambda^2\,, \tag{5.4}$$

$$\frac{dD}{db}=D(\theta-F-2)-4FD\left(\frac{1}{6}\frac{D\Lambda^2}{D\Lambda^2+\gamma}-\frac{1}{4}\right). \tag{5.5}$$

Equation (5.5) has to be considered again as a constraint equation. Assuming γ^* to be of $O(\epsilon)$ we get from $dD/db=0$

$$\theta=2+\tfrac{2}{3}F^*\,. \tag{5.6}$$

The surprise comes from Eq. (5.3). At the fixed point,

$$\theta=6-\frac{2d}{3}\,. \tag{5.7}$$

From Eq. (5.6) we find

$$F^*=6-d\,. \tag{5.8}$$

From Eq. (5.4) we get

$$\frac{\gamma^*}{D\Lambda^2}=\frac{2F^*}{\theta-3F^*}\,. \tag{5.9}$$

Since $\gamma^*/D\Lambda^2$ is $O(\epsilon)$, Eq. (5.9) means that so is F^*. But then Eq. (5.8) means that $d_c=6$! In fact, once F^* is $O(\epsilon)$ it is inferred from Eq. (5.3) that $dc/db>0$ for $d<6$ and vice versa, meaning again that $d_c=6$.

The recursion equations for Q and F are

$$\frac{dF}{db}=(6-d)F+5F^2-3\theta FQ\,, \tag{5.10}$$

$$\frac{dQ}{db}=2Q-2F-\tfrac{7}{3}QF\,. \tag{5.11}$$

The linearized equations are

$$\frac{d\delta F}{db}=5\epsilon\,\delta F-6\epsilon\,\delta Q\,, \tag{5.12}$$

$$\frac{d\delta Q}{db}=(2-\tfrac{7}{3}\epsilon)\delta Q-(2+\tfrac{7}{3}\epsilon)\delta F\,, \tag{5.13}$$

The eigenvalues are found to be

$$\lambda_1=2+\tfrac{11}{3}\epsilon;\quad \lambda_2=-\epsilon\,. \tag{5.14}$$

The critical exponent $\nu=1/\lambda_1$ is now

$$\nu=\tfrac{1}{2}(1-\tfrac{11}{6}\epsilon)\,. \tag{5.15}$$

Evidently, these results are very different from those obtained in Sec. IV. Consequently, the form of the random-force correlation function is very important in determining the critical properties.

Now we turn to the case that $B\neq 0$ but the correlation of the random force is given by Eq. (2.12). When $B\neq 0$, the fixed point found in this section is not consistent. To see this, suppose that $B^*=0(1)$. This is self-contradictory and violates self-similarity because of Eq. (2.33) and the fact that $\gamma^*=O(\epsilon)$. On the other hand, if $B^*=O(\epsilon)$, we cannot have $T^R=T$. Clearly, the fixed point obtained in Sec. IV is not consistent with $B\neq 0$. (Remember that the condition $T^R=K\gamma^R/C^R$ was used, assuming that $B=0$). In fact, we found no way to obtain a stable fixed point, while preserving self-similarity, when $B\neq 0$. We are thus led to claim that the *RG* procedure is consistent with the deterministic result that there is no criticality when $B\neq 0$.

VI. DISCUSSION

The main result of the present analysis is that the critical exponents of the model instability considered above are found to be non-"classical." It is important to stress that such a result cannot be obtained by an analytic expansion of the equations of motion in the distance from the bifurcation point,[11] since the values of the critical exponents indicate that the correct expansion is nonanalytic. In addition, a system size expansion, assuming that the fluctuationg part is smaller by a factor of $1/\sqrt{V}$ compared to the systematic part,[12,13] will not yield these critical exponents since it has been shown above that this scaling is correct only for $d>d_c$. Our results differ also from these predicted by the birth and death master equation in number space.[10] Although we get the same qualitative behavior, i.e., that $\langle Z_{\vec{q}}Z_{-\vec{q}}\rangle \to 0$ and $\langle Z_{\vec{q}}Z_{-\vec{q}}\rangle / \langle\rho\rangle \to \infty$ at the instability, the exponent of the divergence is different. Needless to say, a quasilinear treatment is not capable of finding non-classical exponents. A more critical comparison of the various approaches that appear in the literature to the present one is interesting but is beyond the scope of this paper.

It has been shown that the structure of the random-force autocorrelation function is of great importance in determining the critical behavior. One cannot assume that

$$\langle R(r,t)R(r',t')\rangle = Q\,\delta(r-r')\,\delta(t-t')$$

with Q being a constant. If such an assumption is made the critical dimensionality, as well as all the critical properties, are changed.

The ideas used above are not limited to chemical instabilities. In fact, applications of a similar approach to lasers near threshold, the Benard instability,[14] and the Gunn instability are in progress and will be reported soon.

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APPENDIX

Writing

$$I_{\vec{k}\omega} = \int_{\Lambda/b}^{\Lambda} d^d q \int_{-\infty}^{\infty} d\omega' \left| G^0_{\vec{q},\omega'} \right|^2 G^0_{\vec{k}-\vec{q},\omega-\omega'} \,, \tag{A1}$$

we expand $I_{\vec{k}\omega}$ around $k=0$, $\omega=0$:

$$I_{\vec{k}\omega} = I_{00} + \tfrac{1}{2} \sum_{\alpha\beta} k_\alpha k_\beta \left.\frac{\partial^2 I_{\vec{k}\omega}}{\partial k_\alpha \partial_{k_\beta}}\right|_{\substack{k=0\\ \omega=0}} + \left.\frac{\partial I_{\vec{k}\omega}}{\partial \omega}\right|_{\substack{k=0\\ \omega=0}} \omega \,. \tag{A2}$$

Thus for example I_{00} is

$$I_{00} = \int_{\Lambda/b}^{\Lambda} d^d q \int_{\infty} d\omega \left| G^0_{\vec{q}\omega} \right|^2 G^0_{\vec{q},-\omega} \,. \tag{A3}$$

The frequency part of the integral is done readily, yielding

$$\begin{aligned} I_{00} &= \frac{\pi}{2} \int_{\Lambda/b}^{\Lambda} d^d q \frac{1}{(Dq^2+\gamma)^2} \\ &= \frac{\pi}{2} K_d \int_{\Lambda/b} q^{d-1} dq \frac{1}{(Dq^2+\gamma)^2} \,, \end{aligned} \tag{A4}$$

where K_d is the total spherical angle in d dimensions,

$$K_d = 2^{d-1}\pi^{d/2}\Gamma(d/2) \,. \tag{A5}$$

In the differential renormalization-group technique $b = 1-\delta$, $\delta \to 0$, and thus $\Lambda/b \simeq \Lambda(1+\delta)$. The q integral is then written by inspection. Since the integration interval is infinitesimal, $\delta\Lambda$, we have

$$I_{00} = \delta \frac{\pi}{2} K_d \frac{\Lambda^d}{(D\Lambda^2+\gamma)^2} \,. \tag{A6}$$

The other parts of Eq. (A2) are calculated similarly, with the result Eq. (3.7).

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