Critical Fluctuations of Schlägl’s Chemical Model

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Fluctuations in Schlägl’s \( x^3 \) chemical model near its non-equilibrium critical point are investigated in both the homogeneous and the critical region. Renormalized reaction rates are calculated with the aid of Wilson’s renormalization-group method, and the results are compared with Nicolis and Turner’s classical theory.

§ 1. Introduction

Recently considerable attention has been given to the critical behavior of non-linear systems far from thermal equilibrium and to their analogies to equilibrium critical phenomena. Well-known examples are laser transitions, hydrodynamic instabilities and chemical instabilities.\(^{11-15}\)

Two simple chemical models exhibiting non-equilibrium phase transitions have been presented by Schlägl.\(^3\) Nicolis and Turner\(^5\) have studied spatially-homogeneous fluctuations of Schlägl’s \( x^3 \) model near its non-equilibrium critical point and found that the variance of fluctuations diverges with the classical critical exponent as the critical point is approached. Near the critical point, however, there appears a new characteristic length \( \xi \) which diverges at the critical point, and the diffusion process of spatially-inhomogeneous fluctuations with wavelengths of order \( \xi \) becomes important. Then the property of the fluctuations becomes dependent on the relative magnitude of the inverse length cutoff \( q_c \) to \( \xi^{-1} \).

The cutoff dependence of the fluctuations can be studied by means of the scaling method.\(^7,8\) Mori and McNeil\(^9\) have studied the role of the spatial dimensionality \( d \) and defined the critical dimensionality \( d_c \) above which the fluctuations obey a Gaussian process. They have found that Schlägl’s \( x^3 \) model has \( d_c = 0 \) in the homogeneous region where \( q_c \xi < 1 \) and \( d_c = 4 \) in the critical region where \( q_c \xi \geq 1 \). In this model, however, the variance of fluctuations does not diverge even as the critical point is approached, since the spectral intensity of the fluctuating force vanishes and cancels out the critical slowing-down of the relaxation rate.

The purpose of this paper is to determine the \( d_c \) of Schlägl’s \( x^3 \) model and to investigate its critical fluctuations. A similarity to the kinetic Ising model for equilibrium critical phenomena has been pointed out by Dewel, Walgraef and Boreckmana.\(^9\) We will investigate it in more detail in both the homogeneous and the critical region by determining the spectral intensity of the fluctuating force and
the size of the Ginzburg subregion explicitly.

We briefly summarize a deterministic analysis of Schlögl's $x^3$ model in §2 and the scaling method in §3. In §§4 and 5, we study the critical fluctuations in the homogeneous and the critical region. Section 6 is devoted to a short summary and remarks.

§2. Schlögl's $x^3$ chemical model

As the simplest model exhibiting a non-equilibrium critical point, let us consider the Schlögl model whose reaction scheme is given by

\[ A + 2X \xrightarrow{k_1} 3X, \quad B + X \xrightarrow{k_3} C, \]  

(2.1)

where $k_1$, $k_2$, $k_3$ and $k_4$ denote the reaction rates. The time rate of the concentration of intermediate $X$ is given by

\[ \partial_t x = -k_3 x + k_2 ax^2 - k_4 b x + k_4 c + D\nabla^2 x, \]  

(2.2)

where $a$, $b$ and $c$ are the concentrations of molecules $A$, $B$ and $C$, respectively, which are kept constant in space and time by external control, and $D$ is the diffusion constant.

Let us define $g = k_2$, $y = k_3 a / 3 k_2$ and put $x = u + y$, $k_3 b = \lambda + 3 g y^2$, $k_3 c = (\lambda' + g y^2) y$. Then (2.2) takes the form

\[ \partial_t u = -g y^2 - \lambda u + B + D\nabla^2 u, \]  

(2.3)

where $B = (\lambda' - \lambda) y$. For simplicity let us set $B = 0$ by adjusting $k_4 c$. Then the stable steady solution of (2.3) is given by

\[ u^* = \begin{cases} 0, & \text{if } \lambda > 0, \\ \pm \sqrt{\frac{|\lambda|}{g} / 3}, & \text{if } \lambda < 0, \end{cases} \]  

(2.4a, 2.4b)

where $\lambda > -g y^2$. The stability is determined by linearizing (2.3) around the steady state; putting $u = u^* + u'$,

\[ \partial_t u' = (-\gamma + D\nabla^2) u', \]  

(2.5)

\[ \gamma = \begin{cases} \lambda, & \text{for } u' = 0, \\ 2|\lambda|, & \text{for } u' = \pm (|\lambda| / g)^{1/3}. \end{cases} \]  

(2.6a, 2.6b)

Thus a transition of the second order occurs at $\lambda = B = 0$ and the ordering is given by (2.4) with the linear damping constant (2.6). It is convenient to define the correlation length

\[ \xi = (D / \gamma)^{1/2} = \{D / (3g (u^*)^2 + \lambda)\}^{1/2}, \]  

(2.7)

which diverges at the critical point $\lambda = B = 0$. The foregoing analysis may break
down in the vicinity of the critical point where the fluctuations with wavelengths of order $\xi$ become nonlinear (see § 4B).

§ 3. Fluctuations near the critical point

Let us next consider the fluctuations around the steady state $u'$ near the critical point. The equation of motion is then given by the Langevin equation

$$\partial_t u = D\nabla^2 u - \lambda u + gu^3 + R(r, t).$$

(3.1)

The fluctuating force $R(r, t)$ is assumed to be a Gaussian white noise with

$$\langle R(r, t) \rangle = 0,$$

(3.2)

$$\langle R(r, t) R(r', t') \rangle = 2E(r, r'; u_0) \delta(t - t'),$$

(3.3)

where $\langle \cdots \rangle$ denotes the conditional average over the initial ensemble with the value of $u(r, 0)$ being fixed to be $u_0(r)$. According to Ref. 6) by Mori and McNeil, we have

$$E(r, r'; u) = \{E(u) + D\nabla r \cdot \nabla u\} \delta(r - r'),$$

(3.4)

$$E(u) = 4gy^3(1 + \lambda/4gy^2) + (6gy^2 + \lambda/2)u + 3gyu^2 + gu^3/2.$$

(3.5)

In the vicinity of the critical point $\lambda = B = 0$, we have

$$E(u') = E = 4gy^3.$$

(3.6)

The inverse length and time cutoff of $u(r, t)$ for the space-time coarse graining are denoted by $(q_c, \omega_c)$;

$$u(r, t) = \sum_{q} \int d\omega \langle u(q, \omega) \rangle \exp(-i\omega t),$$

(3.7)

$$|q| \leq q_c, \quad |\omega| \leq \omega_c,$$

(3.8)

where $u(q, \omega)$ is the Fourier component with wavevector $q$ and frequency $\omega$ and $\sum_q$ and $\int d\omega$ denote the sum over wavevectors whose magnitudes are less than the cutoff $q_c$ and the integral over frequencies whose magnitudes are less than $\omega_c$, respectively. The rapidly-varying components have been statistically eliminated and thereby the fluctuating force $R(r, t)$ has been generated. The form of the time evolution of $u(r, t)$ depends upon the relative magnitude of the cutoff $(q_c, \omega_c)$ to the characteristic length and time scales of the system. Therefore, it is important to specify the cutoff explicitly in accordance with the macroscopic observation concerned.

There are two different characteristic regions near the critical point, as indicated in Fig. 1, depending on the relative magnitude of $q_c$ to the inverse correlation length $\xi^{-1}$. HR indicates the homogeneous region where
Fig. 1. Two characteristic regions in the $q_c$ vs. $\xi^{-1}$ diagram near the critical point where $\xi \gg \tau_r$.

$$q_c < \xi^{-1}, \quad \omega_c < \gamma,$$

and CR is the critical region where

$$\xi^{-1} < q_c < \tau_r^{-1}, \quad \tau_r = \omega_c \tau_r^{-1}$$

with $l_r$ and $\tau_r$ being the reaction mean free path and time of molecule $X$. The two regions are characterized by different scalings for the space-time coarse graining. Let us introduce the scale transformation

$$r (\geq q_c^{-1}) \rightarrow L^0 r, \quad t (\geq \omega_c^{-1}) \rightarrow L^0 t,$$

where $L \gg 1$, $\theta \geq 0$. Then, in HR,

$$\xi, \gamma \text{ are fixed,}$$

whereas, in CR,

$$\xi \rightarrow L^{\xi^0}, \quad \gamma \rightarrow L^{-\gamma^0}$$

where $l_r$ and $\tau_r$ are fixed. Each characteristic scaling is useful for extracting the characteristic feature of $u(r, t)$ in each region with the aid of the scaling expansion, i.e., the expansion of $u(r, t)$ in powers of $L^{-1}$.

Let us assume that the scaling exponent of the fluctuating part $\tilde{u} = u - u'$ is positive;

$$\tilde{u} (\equiv u - u') \rightarrow L^{-\beta} \tilde{u}, \quad \beta > 0.$$

Then, in the vicinity of the critical point, (3·4) leads to $E(r, r'; u) \rightarrow L^{-d}E \delta(r - r')$, where $d$ is the spatial dimensionality. Hence the scaling of (3·3) leads to the following scaling of the fluctuating force:

$$R(r, t) \rightarrow L^{-d + \psi \beta} R(r, t).$$

The equation of motion for $\tilde{u}$ is obtained from (3·1);

$$\tilde{\partial}_t \tilde{u} = D\tilde{F}^2 \tilde{u} - \gamma \tilde{u} - 3q u^3 - g\tilde{u}^3 + R(r, t).$$
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Since \( \partial_t \hat{u} \rightarrow L^{-\beta} \partial_t \hat{u} \), balancing \( \partial_t \hat{u} \) with \( R(r, t) \) leads to
\[
\beta = (d-\theta)/2. \tag{3.17}
\]

§ 4. Critical region (\( \xi^{-1} \lesssim q_c \lesssim L^{-1} \))

In this region the cutoff \( (q_c, \omega_c) \) satisfies \( (3.10) \) so that the fluctuations with wavelengths of order \( \xi \) are included in the sum \( (3.7) \). Then \( (3.11) \) and \( (3.13) \) lead to
\[
r(\lesssim q_c^{-1}) \rightarrow Lr, \quad \xi \rightarrow L^{\xi}, \quad l_r \rightarrow l_r,
\]
and the diffusion process will be important, leading to the critical dimensionality \( d_c = 4 \). Therefore, if \( d < 4 \), then as the critical point is approached, there appears a Ginzburg subregion inside which the nonlinear fluctuations are important and outside which the fluctuations obey a Gaussian process. If \( d > 4 \), then the Ginzburg subregion shrinks to zero. Therefore, let us consider the two cases separately.

A. \( d > 4 \)

The constants \( D, \alpha \) and \( g \) are fixed. Hence \( (2.7), (2.6) \) and \( (2.4) \) lead to \( r \rightarrow L^{-2} r, \lambda \rightarrow L^{-\lambda}, t \rightarrow L^\lambda t, u' \rightarrow L^{-\alpha} u' \). \( (\alpha = 1) \). Hence \( \theta = 2 \), and \( (3.17) \) leads to \( \beta = (d-2)/2 \). Therefore \( |\hat{u}| \ll |u'| \) as far as \( d > 4 \), leading to \( d_c = 4 \). Applying the scaling to \( (3.16) \) and taking the most-dominant terms in \( L^{-1} \), we obtain the linear Langevin equation
\[
\partial_t \hat{u} = D \xi^2 \hat{u} - \gamma \hat{u} + R(r, t), \tag{4.2}
\]
which leads to
\[
[\partial_t - D (\partial_r^2 + \partial_r^2 + 2\gamma)] \langle \partial u(r) \partial u(r') \rangle (t) = 2E \beta \langle r - r' \rangle, \tag{4.3}
\]
where \( \partial u(r) \equiv u(r) - \langle u(r) \rangle (t) \). Therefore we obtain, in the limit \( t \rightarrow \infty \),
\[
\langle \partial u(r) \partial u(r') \rangle \approx (E/4\pi D) |r - r'|^{-d+2} \exp[-|r - r'|/\xi]. \tag{4.4}
\]
Let \( X \) be the number of molecules \( X \) in a large volume \( \Omega \). Then, at the critical point \( (\lambda = 0, \xi = \infty) \), \( (4.4) \) leads to the anomalous volume dependence of the variance \( \langle (\partial X)^2 \rangle / \Omega \propto \Omega^d \).

B. Ginzburg subregion (\( d < 4 \))

If \( d < 4 \), then the fluctuations \( \hat{u} \) with wavelengths of order \( \xi \) become of the same order of magnitude as \( u' \) in the ordered state. In fact, taking \( |r - r'| = \xi \) in \( (4.4) \) with \( d = 3 \), we obtain
\[
\hat{u}^3 \sim E/4\pi cD \xi^2 = f|\lambda|^{1/2}, \tag{4.5}
\]
where \( f = E/4\pi cD(D/2)^{1/2} \), and this leads to \( |\hat{u}| \gg |u'| \) if
This condition is also equivalent to $|\lambda| < (fg)^{\frac{1}{2}}$ in the ordered and disordered state. Therefore, in the Ginzburg subregion where (4.6) holds, the fluctuations with wavelengths of order $\xi$ become nonlinear. Then the deterministic analysis of §2 becomes invalid. The nonlinear Langevin equation (3·1), however, is valid if the inverse length cutoff of $u(r,t)$ now denoted by $q_0$ satisfies $\xi^{-1} \ll q_0 \ll l_r^{-1}$, since the microscopic processes determining the reaction rates $k_i$'s do not suffer any change even in the very vicinity of the critical point in strong contrast to equilibrium critical phenomena.

Let us now reduce the inverse length cutoff $q_c$ as $\xi^{-1} \ll q_c \ll q_0$ by eliminating the Fourier components $u(q,w)$ with wavenumbers $q_c < q < q_0$. Then coefficients $D$, $\lambda$, $g$ and the fluctuating force $R(r,t)$ are renormalized by the nonlinear fluctuations with wavelengths of order $\xi$ so that they become cutoff-dependent. This situation is similar to equilibrium critical phenomena. Thus the equation of motion takes the form

$$\partial_t u = Du - \lambda u - gu^3 + R(r,t),$$

where

$$\tilde{\lambda}(q_0, \lambda) = q_0^{\frac{d-2}{2}} f_1(q_0 \xi),$$

$$\tilde{g}(q_0, \lambda) = q_0^{\frac{d-2}{2}} f_2(q_0 \xi)$$

with $\xi \sim |\lambda|^{-\alpha}$. The renormalization is multiplicative with $\zeta > 0$. The cutoff dependence of $D$ and $E$ has been neglected since it is weak. The scaling (4·1) leads to

$$\tilde{\lambda} \to L^{-\alpha} \lambda, \quad \tilde{g} \to L^{-\zeta} \tilde{g},$$

and balancing the five terms of (4·7) leads to

$$\theta = 2, \quad \beta = (d-2)/2,$$

$$\phi = 4 - d, \quad \nu^2 = 2 - \zeta.$$  

(4·10a, 4·10b)

It is worth noting that $u' = (\tilde{\lambda} / \tilde{g})^{\frac{1}{2}} \to L^{-\alpha} u'$ with $\alpha = (d-2)/2 = \beta$. To determine $\lambda$, we have to know the distribution of fluctuations. The nonlinear Langevin equation (4·7) leads to the Fokker-Planck equation whose steady solution $P'(u)$ takes the form

$$\ln P'(u) = -\frac{1}{2E} \int dr \left[ D(u')^2 + \lambda u'^2 + \tilde{g} u'^4 \right].$$

(4·11)

Since this is of the Ginzburg-Landau form, we may use Wilson's renormalization group method. To first order in $\varepsilon = 4 - d$,

$$\zeta = \varepsilon/3, \quad \tilde{\lambda} = (q_0 l_0)^{\frac{d-2}{2}} \lambda,$$

(4·12a)
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\[ \bar{g} = \frac{(8\pi^2 D^2/9E)}{\varepsilon q_0^2}, \]  

(4·12b)

where \( l_0 \) is the microscopic length \( q_0^{-1} \). Since \( \beta > 0 \), \( d \) must be larger than 2. For \( d = 3 \), this leads to \( \beta = 1, \gamma = 1/3, \nu = 5/3 \). The critical exponents are summarized in the second column of Table I, and are similar to the kinetic Ising model for equilibrium critical phenomena. In order of importance, \( D \) and \( E \) become weakly cutoff-dependent.\(^5\) It is also noted that the variance \( \langle (\delta X)^2 \rangle \) at the critical point has the \( \Omega^{1/2} \) dependence which differs from the \( \Omega^{2} \) dependence predicted by Nicolis and Turner.\(^5\)

Outside the Ginzburg subregion where \( |\lambda| > (fg)^2 \), the nonlinear fluctuations are negligible and the classical exponents hold even for \( d = 3 \) when the Ginzburg subregion is sufficiently small, i.e., \( (fg)^2 \ll (D/l_r^2) \), as summarized in the first column of Table I.

Table I. Schrögl's \( x^3 \) model with \( \lambda, (fg)^2 \ll (D/l_r^2) \).

<table>
<thead>
<tr>
<th>Cutoff</th>
<th>CR</th>
<th>HR</th>
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<tbody>
<tr>
<td>( q \xi \geq 1 )</td>
<td>(</td>
<td>\lambda</td>
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<td>( \xi^{-1/3} )</td>
<td>( \xi^{-1/3} )</td>
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<tr>
<td>( \langle u(r)^2 \rangle ) for ( \lambda &lt; 0 )</td>
<td>( \xi^{-1/3} )</td>
<td>( \xi^{-1/3} )</td>
</tr>
<tr>
<td>( \langle \delta u(r) \delta u(r') \rangle ) ( \xi^{-1/3} M(q, \varepsilon) )</td>
<td>( \xi^{-1/3} M(q, \varepsilon) )</td>
<td>( \xi^{-1/3} M(q, \varepsilon) )</td>
</tr>
<tr>
<td>( \langle (\delta X)^2 \rangle / \Omega ) ( \Omega^{1/3} (\varepsilon = \infty) )</td>
<td>( \Omega^{1/3} )</td>
<td>( \Omega^{1/3} )</td>
</tr>
<tr>
<td>( \Gamma_{\text{co}}^{(b)} ) ( \xi^{-3} f(q, \varepsilon) )</td>
<td>( \xi^{-3} f(q, \varepsilon) )</td>
<td>( \xi^{-3} f(q, \varepsilon) )</td>
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</table>

a) This is an approximate expression with \( R = |r' - r| \).

b) The linear relaxation rate of \( u(q, t) \).

\( \xi \)

§ 5. Homogeneous region \( (q \xi \ll \xi^{-1}, l_r^{-1}) \)

This region can be derived from the critical region by eliminating the Fourier components \( u(q, \omega) \) with wavenumbers \( q, \xi \ll \xi^{-1} \). This elimination amounts to putting \( q_r = \xi^{-1} \) in \( \lambda(q_r, \lambda), \bar{g}(q_r) \) and other cutoff-dependent quantities of the critical region similarly to Wilson's procedure for equilibrium critical phenomena.\(^10\) Thus, if \( |\lambda| < (fg)^2 \), then for \( d = 3 \)

\[ \lambda = (\xi/l_0)^{-1/3} \xi^{-2}, \]  

(5·1a)

\[ \bar{g} = 12\pi^2 D^2/9E \xi, \]  

(5·1b)

whereas, if \( |\lambda| > (fg)^2 \), then \( \lambda = \lambda, \bar{g} = g \).

The scaling is given by \((3·11)\) and \((3·12)\):

\( r \ll q_r^{-1} \rightarrow l_r, \xi \rightarrow \xi, l_r \rightarrow l_r \),

(5·2)
where all constants $D$, $E$, $\bar{l}$, $\bar{g}$, etc. are fixed. Hence (4·7), (3·15) and (3·17) give $\theta=0$, $R\rightarrow L^{-d/2}R$, $\beta=d/2$, leading to $d_*=0$. Therefore the fluctuations are linear and the deterministic analysis of § 2 becomes valid if $\lambda$ and $g$ are replaced by $\bar{l}$ and $\bar{g}$, respectively, leading to

$$u'=\pm(\frac{|\bar{l}|}{\bar{g}})^{1/2} \ \text{for} \ \lambda<0,$$

$$\partial_t u = -\bar{\gamma} u + R(r,t),$$

where $\bar{\gamma}=\bar{l} + \bar{g} (u)^3 = D \bar{\gamma}^3$, which is a self-consistent equation for $\bar{\gamma}$. Equations (5·4) and (3·3) lead to

$$\langle \delta u(r) \delta u(r') \rangle^\gamma = \left[ \frac{E}{\bar{\gamma}} \right] \delta (r-r').$$

Thus we obtain the critical exponents summarized in the third and the forth column of Table I.

### § 6. Summary and remarks

We have studied the critical fluctuations of Schlogl's $x^3$ model by investigating the cutoff dependence of the fluctuations with the aid of the scaling method and Wilson's renormalization group method. The scaling exponents obtained are summarized in Table II.

In the homogeneous region where $q_\delta \bar{\gamma} \ll 1$, $\omega_\delta r^{-1} \ll 1$, we have $d_*=0$ and the fluctuations obey a Gaussian Markov process without diffusion, whose critical exponents are summarized in Table I.

In the critical region where $q_\delta \bar{\gamma} \gtrsim 1$, $\omega_\delta r^{-1} \gtrsim 1$, however, the diffusion process becomes important, leading to $d_* = 4$. Then if $d = 3$, there appears a Ginzburg subregion inside which the fluctuations are non-Gaussian with the non-classical critical exponents summarized in the second column of Table I. Outside this subregion, the fluctuations are Gaussian and their critical behaviors are described by the classical exponents summarized in the first column of Table I, if the Ginzburg subregion is sufficiently small.

Equations (3·1) and (4·7) have the same form as the stochastic Ginzburg-Landau equation for the order parameter. This type of stochastic equation very often appears in the neighborhood of non-equilibrium, as well as equilibrium, critical points. In this respect, Schlogl's $x^3$ model gives a significant model. The property of the fluctuating force $R(r,t)$, however, depends on its origin. In partic-
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ular, in the case of non-equilibrium critical points, a stochastic Ginzburg-Landau type equation is obtained by eliminating irrelevant macrovariables other than an order parameter. Then the fluctuating force generated by the elimination and its spectral intensity $E(u')$ have a strong dependence on the order parameter even in the very vicinity of the critical point, thus leading to a quite different scaling from (3.15). This gives an important difference from equilibrium critical phenomena, as will be discussed in a separate paper.

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