ON THE CRITICAL BEHAVIOUR OF THE SCHLÖGL MODEL

M.E. BRACHET
Physique Théorique, Université Paris VI, France

and

E. TIRAPEGUI
Institutt voor Theoretische Fysica, B-3030 Leuven, Belgium

Received 28 August 1980

The critical behaviour of the Schlögl model is studied using field theoretical methods. It is shown that for the equal time correlation functions this behaviour is that of the well-known $g\varphi^4$ model.

We shall give here a field theoretical treatment of a well-known model in chemical reactions: the Schlögl model. The reaction is

$$A + 2X \underset{k_2}{\overset{k_1}{\rightleftharpoons}} 3X\,, \quad X \underset{k_4}{\overset{k_3}{\rightleftharpoons}} B\,, \tag{1}$$

where the concentrations of A and B are kept constant. In order to make a local study of (1) we establish a master equation in which we treat the chemical part as a birth and death process and the diffusion contribution as a random walk. For the chemical part we impose the extensivity of the transition probabilities. One first divides the space in cells of volume V and calling N_r the number of molecules X in the cell with position vector $\boldsymbol{r}$ one writes down a multivariate master equation for the probability density $P[\{N_r\}, t]$ [1]. From this master equation one can obtain a functional Fokker–Planck equation for the probability density $p[n(\boldsymbol{r}), t]$, where $n(\boldsymbol{r})$ is now the concentration at the point $\boldsymbol{r}$. That one expects to obtain a correct description of the system below and at the bifurcation point has been shown in refs. [2,3]. The Fokker–Planck equation is ($p[n(\boldsymbol{r}), t]$ is of course a functional of $n(\boldsymbol{r})$):

$$\begin{aligned}\dot{p}[n(\boldsymbol{r}), t] = \Bigg\{ &\int \mathrm{d}\boldsymbol{r}' \frac{\delta}{\delta n(\boldsymbol{r}')} [\mu(n(\boldsymbol{r}')) - \lambda(n(\boldsymbol{r}')) - D\nabla^2 n(\boldsymbol{r}')] \\ &+ \frac{1}{2}\int \mathrm{d}\boldsymbol{r}'\,\mathrm{d}\boldsymbol{r}'' \frac{\delta}{\delta n(\boldsymbol{r}')} \frac{\delta}{\delta n(\boldsymbol{r}'')} \{[\mu(n(\boldsymbol{r}')) + \lambda(n(\boldsymbol{r}''))]\,\delta(\boldsymbol{r}' - \boldsymbol{r}'') \\ &+ 2D\boldsymbol{\nabla}_{r'} \cdot \boldsymbol{\nabla}_{r''}\,\delta(\boldsymbol{r}' - \boldsymbol{r}'')\,n(\boldsymbol{r}')\}\Bigg\}\, p[n(\boldsymbol{r}), t]\,,\end{aligned} \tag{2}$$

where in $\mu - \lambda$ terms up to $O(1/v)$ should be kept while in $\mu + \lambda$ these terms can be omitted. Here $\mu(n)$ is the probability of death and $\lambda(n)$ that of birth, and D is the Fick diffusion constant. Using the usual parametrization (which involves fixing the unit of time) one has [4],

$$\mu - \lambda = n^3/a^2 - 3n^2/a + (3+\delta)n - (1+\delta')a \,, \tag{3}$$

$$\mu + \lambda = n^3/a^2 + 3n^2/a + (3+\delta)n + (1+\delta')a \,, \tag{3'}$$

where a is the concentration of A, and δ and δ' are dimensionless numbers. The deterministic equation is

$$dn/dt = \lambda(n) - \mu(n) \,. \tag{4}$$

To treat the problem we can now introduce an operator formalism and a functional integral formalism as we have explained in ref. [5]. Writing the transition probability density $P[n(\boldsymbol{r}), t \,|\, n_0(\boldsymbol{r}), t_0]$ as $\langle n(\boldsymbol{r})|U(t,t_0)|n_0(\boldsymbol{r})\rangle$, one obtains for the evolution operator $U(t,t_0)$ the equation $\mathrm{i}\partial U(t,t')/\partial t = \hat{H}U(t,t')$, $U(t,t) = 1$, where the "hamiltonian" $\hat{H}$ is obtained from eq. (2) by the usual replacements $-\mathrm{i}\delta/\delta n(\boldsymbol{r}) \to \hat{\pi}(\boldsymbol{r})$, $n(\boldsymbol{r}) \to \hat{n}(\boldsymbol{r})$. These operators satisfy the usual commutation relations

$$[\hat{n}(\boldsymbol{r}), \hat{n}(\boldsymbol{r}')] = [\hat{\pi}(\boldsymbol{r}), \hat{\pi}(\boldsymbol{r}')] = 0 \,, \quad [\hat{n}(\boldsymbol{r}), \hat{\pi}(\boldsymbol{r}')] = \mathrm{i}\delta^{(d)}(\boldsymbol{r}-\boldsymbol{r}') \,.$$

The hamiltonian $\hat{H}$ has a chemical part $\hat{H}_c$ and a diffusion part $\hat{H}_D$, $\hat{H} = \hat{H}_c + \hat{H}_D$, given by

$$\hat{H}_c = \int d\boldsymbol{r}\, \mathcal{H}_c$$
$$= -\int d\boldsymbol{r}\, \hat{\pi}(\boldsymbol{r})[\mu(\hat{n}(\boldsymbol{r})) - \lambda(\hat{n}(\boldsymbol{r}))] - \tfrac{1}{2}\mathrm{i}\int d\boldsymbol{r}\, d\boldsymbol{r}'\, \hat{\pi}(\boldsymbol{r})\hat{\pi}(\boldsymbol{r}')[\mu(\hat{n}(\boldsymbol{r})) + \lambda(\hat{n}(\boldsymbol{r}'))]\delta^{(d)}(\boldsymbol{r}-\boldsymbol{r}') \,, \tag{5}$$

$$\hat{H}_D = \int d\boldsymbol{r}\, \mathcal{H}_D = D\int d\boldsymbol{r}\, \hat{\pi}(\boldsymbol{r})\nabla^2\hat{n}(\boldsymbol{r}) - \mathrm{i}\int d\boldsymbol{r}\, d\boldsymbol{r}'\, \hat{\pi}(\boldsymbol{r})\hat{\pi}(\boldsymbol{r}')\boldsymbol{\nabla}_{\boldsymbol{r}} \cdot \boldsymbol{\nabla}_{\boldsymbol{r}'}\delta^{(d)}(\boldsymbol{r}-\boldsymbol{r}')\hat{n}(\boldsymbol{r}) \,, \tag{6}$$

where d is the dimension of space. Putting $\delta = \delta' > 0$ we have from eq. (4) the stationary state $n(\boldsymbol{r}) = a$ which is a simple root of $(\lambda - \mu)(n) = 0$ for $\delta > 0$, and a triple root for $\delta = 0$ (the critical point). We are interested in the field $\phi(\boldsymbol{r}) = n(\boldsymbol{r}) - a$, consequently we make this translation in (5) and (6) to obtain

$$\hat{H}_c = -\int d\boldsymbol{r}\, \hat{\pi}[\hat{\varphi}^3/a^2 + \delta\hat{\varphi}] - \tfrac{1}{2}\mathrm{i}\int d\boldsymbol{r}\, \hat{\pi}^2[\hat{\varphi}^3/a^2 + 6\hat{\varphi}^2/a + (12+\delta)\hat{\varphi} + a(8+2\delta)] \,, \tag{7}$$

$$\hat{H}_D = \int d\boldsymbol{r}\, D[\hat{\pi}\nabla^2\hat{\varphi} - \mathrm{i}(\nabla\hat{\pi})^2 a - \mathrm{i}(\nabla\hat{\pi})^2\hat{\varphi}] \,. \tag{8}$$

The correlation functions are generated by a functional derivation $\delta/\delta j(t,\boldsymbol{r})$ of the generating functional ($\gamma_1(0)$ stands for prepoint discretization [6]):

$$Z[j,j^*] = \int_{\gamma_1(0)} \mathcal{D}\varphi\, \mathcal{D}\pi \exp\left\{\mathrm{i}\int d\tau\, d\boldsymbol{r}\, [\pi(\tau,\boldsymbol{r})\dot{\varphi}(\tau,\boldsymbol{r}) - \mathcal{H} + j\varphi + j^*\pi]\right\} \,, \tag{9}$$

where $\mathcal{H} = \mathcal{H}_c + \mathcal{H}_D$, and is read directly from (7) and (8). Splitting off the quadratic part $\mathcal{H}_0$ in order to generate the perturbation expansion we write $\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_I$ with

$$\mathcal{H}_0 = D\pi\nabla^2\varphi - \delta\pi\varphi - \tfrac{1}{2}\mathrm{i}\,a(8+2\delta)\pi^2 \,, \tag{10}$$

$$\mathcal{H}_I = -\mathrm{i}aD(\nabla\pi)^2 - \mathrm{i}D(\nabla\pi)^2\varphi - \pi\varphi^3/a^2 - \tfrac{1}{2}\mathrm{i}\pi^2[\varphi^3/a^2 + 6\varphi^2/a + (12+\delta)\varphi] \,. \tag{11}$$

The perturbation expansion is generated by writing

$$Z[j,j^*] = \exp\left[-\mathrm{i}\int d\tau\, d\boldsymbol{r}\, \mathcal{H}_I\right]\Bigg|_{\varphi=(1/\mathrm{i})\delta/\delta j,\, \pi=(1/\mathrm{i})\delta/\delta j^*} \cdot Z_0[j,j^*] \,, \tag{12}$$

with

$$Z_0[j,j^*] = \int \mathcal{D}\varphi\, \mathcal{D}\pi \exp\left\{ i \int d\tau\, d\boldsymbol{r}\, [\pi\dot{\varphi} - D\pi\nabla^2\varphi + \delta\pi\varphi + ia(4+\delta)\pi^2 + j\varphi + j^*\pi] \right\}. \tag{13}$$

We compute $Z_0[j,j^*]$ in order to have the propagators in the stationary case and we obtain:

$$Z_0[j,j^*] = \exp\left[-\frac{1}{2} \int dx'\, dx''\, j(x')\Delta(x'-x'')j(x'') - \int dx'\, dx''\, j^*(x')S(x'-x'')j(x'') \right], \tag{14}$$

with ($k\cdot x = t - \boldsymbol{k}\cdot\boldsymbol{x}$)

$$S(k) = (2\pi)^{-(d+1)}[\omega - iDk^2 - i\delta]^{-1}, \tag{15}$$

$$\Delta(k) = (2\pi)^{-(d+1)} a(8+2\delta)/[\omega^2 + (\delta + Dk^2)^2], \tag{16}$$

where $S(x) = \int dk \exp(ik\cdot x)S(k)$, $\Delta(x) = \int dk \exp(ik\cdot x)\,\Delta(k)$. In the Feynman rules obtained from (12), (15) and (16) one should recall that there is a natural cut-off for big $|\boldsymbol{k}|$ due to the finite volume of the original cells. The correlation function $\langle\phi(t',\boldsymbol{r}')\phi(t,\boldsymbol{r})\rangle$ is given by

$$\langle\varphi'\varphi\rangle = -[\delta^2/\delta j(t',\boldsymbol{r}')\delta j(t,\boldsymbol{r})]\, Z[j,j^*]\,|_{j=j^*=0}\,. \tag{17}$$

One should note that the loop expansion here is an expansion in powers of the dimensionless quantity $(aD^{d/2})^{-1}$. One can easily check by power counting that the critical dimension of the model is $d_c = 4$, and moreover that at $d = 4 - \epsilon$ the only relevant coupling for the infrared behaviour (we are interested in the long range behaviour of $\langle\phi'\phi\rangle$) is $-\pi\phi^3/a^2$. This means that we can use a new generating functional $Z[j,j^*]$ to obtain the dominant infrared behaviour. One has

$$Z[j,j^*] = \int \mathcal{D}\varphi\, \mathcal{D}\pi \exp\left\{ i \int d\tau\, d\boldsymbol{r}\, [\pi\dot{\varphi} - D\pi\nabla^2\varphi + \delta\pi\varphi + ia(4+\delta)\pi^2 + \pi\varphi^3/a^2 + j\varphi + j^*\pi] \right\}. \tag{18}$$

This now corresponds to a new Fokker–Planck equation with constant diffusion, which is

$$\dot{p}[\varphi,t] = -\int d\boldsymbol{r}\, (\delta/\delta\varphi(\boldsymbol{r}))[D\nabla^2\varphi - \delta\varphi - \varphi^3/a^2 - (\delta/\delta\varphi)a(4+\delta)]\, p[\varphi,t]\,. \tag{19}$$

The conditions of detailed balance are now satisfied by eq. (19) and this implies that the stationary solution can be computed as a solution of

$$\delta p_{st}[\varphi]/\delta\varphi = [a(4+\delta)]^{-1}[D\nabla^2\varphi - \delta\varphi - \varphi^3/a^2], \tag{20}$$

whose solution is (N is a normalization factor):

$$p_{st}[\varphi] = N \exp\left\{ -[D/a(4+\delta) \int d\boldsymbol{r}\, [\tfrac{1}{2}(\nabla\varphi)^2 + \tfrac{1}{2}\delta D^{-1}\varphi^2 + \varphi^4/4a^2D] \right\}. \tag{21}$$

We can still make a scaling of the field ϕ as $\phi' = [D/a(4+\delta)]^{1/2}\phi$ to obtain

$$p_{st}[\varphi'] = N \exp\left\{ -\int d\boldsymbol{r}\, [\tfrac{1}{2}(\nabla\varphi')^2 + \tfrac{1}{2}\delta D^{-1}\varphi'^2 + g_0\varphi'^4] \right\}, \tag{22}$$

with $g_0 = (4+\delta)/4aD^2$. This shows then that the critical behaviour of the equal time correlation function $\langle\phi(t,\boldsymbol{r}')\phi(t,\boldsymbol{r})\rangle$ is determined by the known critical behaviour of the ϕ^4 model [7], a result that has also been obtained in ref. [1], see also ref. [8]. This means that at the critical point one has a long range correlation function behaving in dimension 3 as $(|\boldsymbol{r} - \boldsymbol{r}'|^{1+\eta})^{-1}$, where η is a known critical exponent. The methods used here can of course be applied to more general chemical reactions.

References

[1] M. Malek-Mansour, C. van den Broeck, G. Nicolis and J.W. Turner, Asymptotic properties of markovian master equations, preprint Univ. Libre de Bruxelles (1980).
[2] W. Horsthemke and L. Brenig, Z. Phys. B27 (1977) 341.
[3] W. Horsthemke, M. Malek-Mansour and L. Brenig, Z. Phys. B28 (1977) 135.
[4] G. Nicolis and J.W. Turner, Physica 89A (1977) 245.
[5] F. Langouche, D. Roekaerts and E. Tirapegui, Physica 92A (1979) 252.
[6] F. Langouche, D. Roekaerts and E. Tirapegui, Phys. Rev. D20 (1979) 419; Prog. Theor. Phys. 60 (1979) 1617.
[7] E. Brézin, J.C. Le Guillou and J. Zinn-Justin, Field theoretical approach to critical phenomena in phase transitions and critical phenomena, Vol. 6, eds. C. Domb and M.S. Green (Academic Press, 1976).
[8] G. Dewel, D. Walgraaf and P. Borckmans, Z. Phys. B28 (1977) 235.