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DIFFUSION IN BINARY SYSTEMS IN A CRITICAL STATE

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Аннотация—Предлагается феноменопогическая теория переноса массы в бинарных системах вблизи критической точки.

NOMENCLATURE

c, concentration;
c^*, critical concentration;
μ, chemical potential;
j, mass flow;
D_i, phenomenological coefficients of "diffusion".

1. The diffusion coefficient in a binary mixture defined as the proportionality factor between a mass flow and concentration gradient is, as is known, directly proportional to the derivative $(\partial\mu/\partial c)_{p,T}$ which vanishes at a critical point [1].

In its turn, the numerous experiments [2] have established that the concentration gradients in binary mixtures at the critical state do not lead to mass transfer for a long period of time. Sometimes this is named as the disappearance of diffusion at the critical point.

Note that according to the definition of a critical point the second derivative $(\partial^2\mu/\partial c^2)_{p,T}$ also vanishes there, hence, in the vicinity of the critical point the diffusion coefficient depends upon concentration as:

$$D \sim (c - c^*)^2$$

where c^* is the critical concentration.

2. From the phenomenological viewpoint the equality of the diffusion coefficient to zero at the critical point means that the ordinary expression for a flow (the Fick law)

$$\vec{j} = -D\nabla c \qquad (1)$$

in the vicinity of the critical point appears to be insufficient. In order to obtain a correct relation between the flow and the concentration distribution it is natural to take into consideration the following (after [1]) terms in flow expansion in a power series of the relative change of concentration for some characteristic molecular length†. Under ordinary conditions these terms are negligibly small. However, at a critical point where the "ordinary" diffusion flow disappears, the whole mass transfer will be defined by these terms. In the approximation following, the mass flow may be represented as the sum

$$\vec{j} = -D\nabla c + D_1\nabla(\Delta c) + D_2\nabla(\nabla c)^2 + D_3(\nabla c)^2\nabla c, \qquad (2)$$

where D_i are some coefficients which at the critical point differ from zero and $D = D_0(c - c^*)^2$ if the concentration is sufficiently close to the critical one.

The relative values of the terms in equation (2) may be estimated only from dimensional considerations in the phenomenological theory. Such an estimate is not difficult and leads to the conclusion that in any case the fourth term in (2) is much smaller than the first, and the third is much smaller than the second (of course, here we are talking about a macroscopic problem so that the characteristic dimension of a substance distribution, L, is much greater than the molecular length, l). Indeed, for the four summands

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† In gases the mean free path is a characteristic length. In the case under consideration the correlation length may serve as the characteristic molecular length.

entering the right-hand side of (2) there are appropriate estimates

$$\begin{aligned} |j_0| &\sim A_0 \left(\frac{\delta c}{c^*}\right)^2 \frac{l}{L}\,\delta c\cdot v \\ |j_1| &\sim A_1 \left(\frac{l}{L}\right)^3 \delta c\cdot v \\ |j_2| &\sim A_2 \frac{\delta c}{c^*}\left(\frac{l}{L}\right)^3 \delta c\cdot v \\ |j_3| &\sim A_3 \left(\frac{\delta c}{c^*}\right)^2 \left(\frac{l}{L}\right)^3 \delta c\cdot v, \end{aligned} \tag{3}$$

where δc are the characteristic changes (drop) in concentration; v is the characteristic molecular velocity, and A_i are dimensionless coefficients. Within the framework of the phenomenological theory it is natural to assume that the latter coefficients are of the same order of magnitude. Since the concentrations under consideration are close to the critical ones, $\delta c/c^* \ll 1$, and besides $l/L \ll 1$, it immediately follows from the estimates of (3) that

$$|j_0| \gg |j_3|$$

and (4)

$$|j_1| \gg |j_2|,$$

as already stated above

Taking into account the latter estimates and using the continuity equation for c, we come to the following diffusion equation valid in the vicinity of the critical point:

$$\frac{\partial c}{\partial t} = \mathrm{d}iv\{D_0 c^2 \nabla c - D_1 \nabla(\Delta c)\}, \tag{5}$$

where for convenience concentration is recorded from the critical one. The diffusion equation at $D_0 = 0$ was considered for the first time in [3]. Of course this equation is valid only exactly at the critical point.

We note that nevertheless, in some works the diffusion equation was studied which did not contain the term with D_1 which is basic at a critical point has been however investigated (see, for example [4]).

Mark that proceeding from the condition of the entropy increase it follows that in the vicinity of a critical point the coefficient $D_1 > 0$. In addition, as it will be shown later, the latter inequality is a necessary condition for the existence of the steady-state solutions of the diffusion equation (5).

3. Consider the simplest boundary problems of equation (5). First of all, let us examine the steady-state problems. Many steady-state boundary-value problems which are interesting from the physics point of view have trivial solutions of the form c = const.

One of the problems with a non-trivial steady-state distribution of concentration is the boundary-value problem for a semi-infinite region $(0 \leqslant x < \infty)$

$$\frac{\mathrm{d}^4 c}{\mathrm{d}x^4} - \frac{D_0}{D_1}\frac{\mathrm{d}}{\mathrm{d}x}\left(c^2 \frac{\mathrm{d}c}{\mathrm{d}x}\right) = 0, \tag{6}$$

$$c(0) = c_0. \tag{7}$$

At $x = \to \infty$ it is assumed that $c(x)$ and the necessary number of its derivatives vanish.

The solution of this boundary-value problem is, as it can easily be checked

$$c(x) = \frac{c_0}{1 + x/x_0}, \tag{8}$$

here

$$x_0 = \left[c_0 \sqrt{\left(\frac{D_0}{6D_1}\right)}\right]^{-1}. \tag{9}$$

The condition for the solution is $D_0/D_1 > 0$ and since always $D_0 > 0$, then it follows that also $D_1 > 0$ as has been mentioned at the end of the previous chapter.

From the properties of the solution (8) we only note that

$$\int_0^\infty c(x)\,\mathrm{d}x$$

diverges. This means that an infinite amount of substance must be introduced into the region under consideration before steady state is established.

4. Let us study the solution of equation (5) in the simplest case of an infinite one-dimensional region.

The equation has the form

$$\frac{\partial c}{\partial t} = D_0 \frac{\partial}{\partial x}\left(c^2 \frac{\partial c}{\partial x}\right) - D_1 \frac{\partial^4 c}{\partial x^4}. \tag{10}$$

From the point of view of physics, of interest will be the even solutions, with respect to x, which decrease sufficiently for $x \to \pm\infty$, so that the following integral exists

$$\int_{-\infty}^{\infty} c(x, t)\,\mathrm{d}x = q = \text{const.} \tag{11}$$

As readily seen, problem (10)–(11) possesses a similarity property. Its solution may be sought in the form:

$$c(x, t) = \left(\frac{D_1}{4D_0^2 t}\right)^{\frac{1}{4}} f(\xi), \tag{12}$$

$$\xi = \frac{x}{(4D_1 t)^{\frac{1}{4}}},$$

where the function of $f(\xi)$ satisfies the differential equation of the third order (one integration is performed simply):

$$f''' - f^2 f' - \xi f = 0. \tag{13}$$

Condition (5) assumes the form:

$$\int_0^{\infty} f(\xi)\,\mathrm{d}\xi = Q, \tag{14}$$

where

$$Q = \frac{q}{4}\sqrt{\left(\frac{D_0}{2D_1}\right)}.$$

The law of motion for the points of equal concentration $x \sim t^{\frac{1}{4}}$ is the essential consequence resulting from the similar solution of equation (12); thus diffusion at a critical point occurs slower than ordinary diffusion ($x \sim t^{\frac{1}{2}}$). This is also valid for the case of a larger number measurements.

5. Let us investigate some properties of the solution of equation (13). For small values of the parameter Q the solution of equation (13) will be arbitrarily close to that of the linear equation

$$f''' - \xi f = 0. \tag{15}$$

Under the condition (14) the solution of the latter equation is given by the integral

$$f(\xi) = \frac{2}{\pi} Q \int_0^{\infty} \exp\left[-(z^4/4)\right] \cdot \cos(\xi z)\,\mathrm{d}z. \tag{16}$$

The function $f(\xi)$ oscillates assuming positive and negative values since according to the Laguerre theorem [5] the entire function (16) has an infinite number of real zeros (and no complex ones). The asymptotic behaviour of the function $f(\xi)$ defined according to equation (16) may be obtained by the method of steepest descent. The steepest descents of the integral of (16) are located at points

$$z_1 = \frac{\sqrt{3} + i}{2}\xi^{\frac{1}{3}}, \qquad z_2 = -\frac{\sqrt{3} - i}{2}\xi^{\frac{1}{3}},$$

$$z_3 = -i\xi^{\frac{1}{3}}.$$

(See Fig. 1.) It is possible to show that the asymptotic behaviour of the integral (16) is defined only by the sum of the contributions of the points z_1 and z_2 which lie in the upper half plane. The path of the integration in the vicinity of these points is determined by the equalities

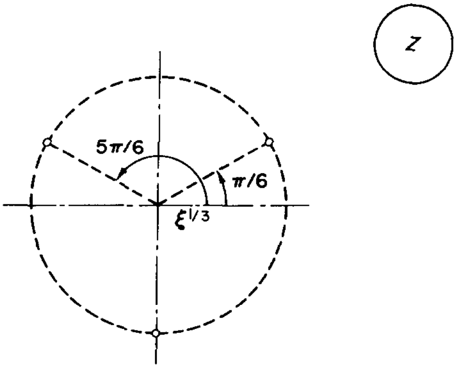

FIG. 1. Position of points of steepest descent (16).

$$\operatorname{Im}\left(i\xi z - \frac{z^4}{4}\right) = \operatorname{Im}\left(i\xi z_k - \frac{z_k^4}{4}\right)(k = 1, 2),$$

respectively. Consequently, the asymptotic behaviour of the function predetermined by the integral (16) will be of the form

$$f(\xi) \simeq 2 \sqrt{\left(\frac{2}{3\pi}\right)} Q \exp\left[-\tfrac{3}{8}\xi^{\frac{4}{3}}\right] \cdot \frac{\cos\{[3(\sqrt{3})/8]\,\xi^{\frac{4}{3}} - (\pi/6)\}}{\xi^{\frac{1}{3}}} \qquad (17)$$

Note that since $f(\xi) \to 0$ at $\xi \to \infty$ the solution of (16) and (17) will also be valid for any Q if only the values of ξ are sufficiently great.

This case physically corresponds to the transfer process with concentrations which are very close to the critical ones when "ordinary" diffusion is unessential due to the small diffusion coefficient.

On the other hand, for sufficiently great values of Q there always exists such a region of the values of ξ when ordinary diffusion is the basic mechanism of transfer. It is not difficult to show that in this region the derivative f''' in equation (13) is negligibly small, and the solution has the form of the known thermal waves of Zeldovich–Kompanieets [6, 7]:

$$f(\xi) = \begin{cases} \sqrt{(\xi_0^2 - \xi^2)} & \text{for } \xi < \xi_0, \\ 0 & \text{for } \xi > \xi_0, \end{cases} \qquad (18)$$

It goes without saying that the solution of (18) is not true for ξ close to (or greater than) ξ_0, since with a decrease of the function $f(\xi)$ the relative role of the third derivative in (13) increases, and the solution assumes the form of (16).

The regions where the solutions of (16) and (18) are valid are joined by a transition region in which

$$\xi \sim \xi_0 \sim \sqrt{Q}. \qquad (19)$$

Actually the whole diffusing substance is concentrated in the region where $\xi < \xi_0$.

The results of the numerical solution of the complete equation (13) for $Q = 1$ and 50·4 are given in Tables 1 and 2, respectively.

Thus, for the concentration distribution we have two quite distinct regions (see Fig. 2 curves 1 and 2): the region of small ξ with a distribution of the type of a thermal wave (18) and that of large ξ where the solution has the form of damped oscillations (16).

Table 1. $Q = 1$

ξ	$f(\xi)$	ξ	$f(\xi)$	ξ	$f(\xi)$
0	0·7893	2·2	0·0680	4·4	−0·0193
0·2	0·7796	2·4	0·0137	4·6	−0·0083
0·4	0·7489	2·6	−0·0278	4·8	0·0003
0·6	0·7002	2·8	−0·0565	5·0	0·0062
0·8	0·6357	3·0	−0·0735	5·2	0·0097
1·0	0·5589	3·2	−0·0803	5·4	0·0112
1·2	0·4738	3·4	−0·0788	5·6	0·0109
1·4	0·3846	3·6	−0·0712	5·8	0·0095
1·6	0·2957	3·8	−0·0596	6·0	0·0075
1·8	0·2112	4·0	−0·0460		
2·0	0·1344	4·2	−0·0321		

Table 2. $Q = 50·4$

ξ	$f(\xi)$	ξ	$f(\xi)$	ξ	$f(\xi)$
0	8·0000	3·6	7·1442	7·2	3·4588
0·2	7·9975	3·8	7·0398	7·4	3·0081
0·4	7·9899	4·0	6·9281	7·6	2·4931
0·6	7·9775	4·2	6·8087	7·8	1·9161
0·8	7·9599	4·4	6·6812	8·0	1·3044
1·0	7·9372	4·6	6·5450	8·2	0·7236
1·2	7·9095	4·8	6·3997	8·373	0
1·4	7·8765	5·0	6·2446	8·4	−0·0480
1·6	7·8384	5·2	6·0789	8·6	−0·2326
1·8	7·7949	5·4	5·9017	8·8	−0·2759
2·0	7·7459	5·6	5·7120	9·0	−0·2129
2·2	7·6916	5·8	5·5084	9·2	−0·1287
2·4	7·6315	6·0	5·2892	9·4	−0·0576
2·6	7·5657	6·2	5·0522	9·6	−0·0121
2·8	7·4940	6·4	4·7947	9·6797	0
3·0	7·4162	6·6	4·5128	9·8	0·0112
3·2	7·3321	6·8	4·2013		
3·4	7·2415	7·0	3·8530		

6. The above phenomenological approach to mass-transfer phenomena near the critical point and the derived equation (3) make it possible to consider particular boundary-value problems, corresponding to various experimental conditions. However, let us emphasise that the simple boundary-value problems considered here allow

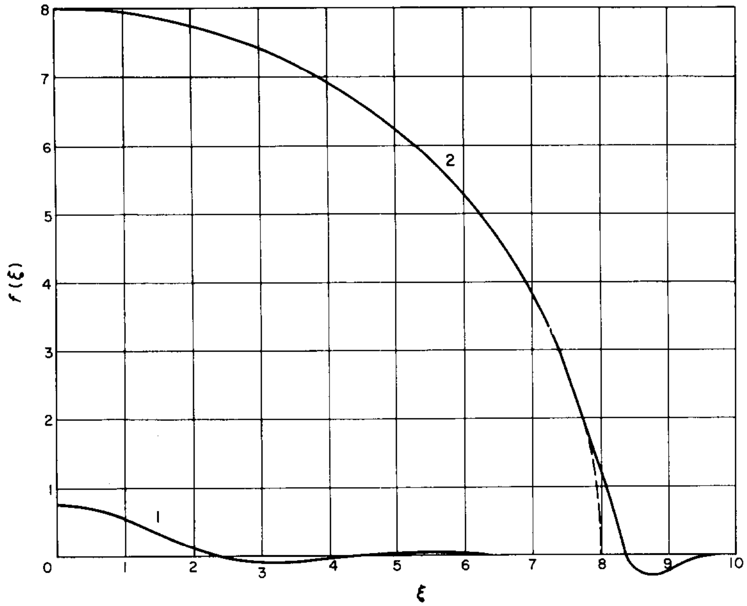

FIG. 2. Curve 1: numerical solution of equation (13) for $Q = 1$. Curve 2: numerical solution of equation (13) for $Q = 50{\cdot}4$, solid curve; solution of type "thermal wave" (18), dashed line.

a very clear explanation of the main peculiarities of mass-transfer phenomena in the critical region.

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Abstract—The phenomenological theory is proposed of mass transfer in binary systems near the critical point.

Résumé—On propose une théorie phénoménologique du transport de masse dans des systèmes binaires au voisinage du point critique.

Zusammenfassung—Für den Stofftransport in binären Systemen nahe dem kritischen Punkt wird eine phänomenologische Theorie vorgeschlagen.