ON DIFFUSION IN THE CRITICAL DOMAIN

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An approach permitting the construction of approximate solutions of problems for the non-linear nonstationary critical diffusion equation in a space domain of arbitrary geometry is proposed.

Measurements in the critical domain have disclosed not only the extremely slow progress of diffusion processes in this domain [1–4] but also that they proceed in two stages in time [5] together with the laminar structure of the diffusion streams in binary liquid solutions [6]. The singularities mentioned are not included in the classical Fick diffusion equation, and this was a stimulus to derive a more exact critical diffusion equation. Thus, for example, an equation based on an analysis of the correlation between the fluctuations in component concentrations in a binary solution in the critical domain is contained in [7]. The equation from [7] permitted an explanation of the laminar configuration of the diffusion streams in direct proximity to the critical point. Later [8], the domain of applicability of this equation was extended by adding a nonlinear term. A rather different kind of nonlinear term, which more adequately describes the expansion of the diffusion stream in powers of the relative change in concentration is proposed in [9]. Consequently, the critical diffusion equation taking account of the effect of spatial dispersion and the nonlinearity of terms in the diffusion stream expansion permitted the description of not only the laminar configuration but also the two-stage progress of the critical diffusion processes.

The equation obtained in [9] for a two-component mixture without taking its nonisothermy and the nonlinear convective effects into account and being of the form

$$\frac{\partial u}{\partial t} = A \operatorname{div}(u^2 \nabla u) - H \Delta \Delta u, \quad u = c - c_{\mathrm{cr}}, \tag{1}$$

is valid for diffusion not only near the critical points of solutions, but also in the domain of the liquid–vapor critical points, as well as in the neighborhood of phase transitions of the second kind since it takes account of the magnification of the correlation between the density fluctuations in this case.

In contrast to [9], we tried to solve the complete three-dimensional equation (1) for a space domain of arbitrary geometry. The idea of the solution proposed is first to linearize (1) and later to take account of the linearization errors as perturbing functions in the successive approximations of the perturbation method. The solution of the linearized (unperturbed) problem is hence constructed on the basis of the integral method of Tolubinskii [10], which permits the Green's function of the heat conduction equation to be obtained in a domain of arbitrary shape by means of the known fundamental solution of this equation.

To linearize (1), let us use the method proposed in [11] for the heat conduction equation. With respect to the function $\varphi = u^2$ we can rewrite (1) as

$$\frac{\partial u}{\partial \varphi} \frac{\partial \varphi}{\partial t} = A \operatorname{div}\left(\varphi \frac{\partial u}{\partial \varphi} \nabla \varphi\right) - H \Delta \left[\frac{\partial^2 u}{\partial \varphi^2}(\nabla \varphi)^2 + \frac{\partial u}{\partial \varphi} \Delta \varphi\right]. \tag{2}$$

If we put

$$\varphi \frac{\partial u}{\partial \varphi} = C + \varepsilon \theta_1(\varphi), \quad \frac{\partial u}{\partial \varphi} = B + \varepsilon \theta_2(\varphi), \tag{3}$$

in (2), where ε $(0 \le \varepsilon \le 1)$ is a perturbation parameter and B and C are some constants, then we obtain an equation transformed relative to φ, which is identical to the initial equation for the value $\varepsilon = 1$

$$L(\varphi, \varepsilon) = B \frac{\partial \varphi}{\partial t} - AC \operatorname{div}(\nabla\varphi) + BH\Delta\Delta\varphi + \varepsilon\Phi(\varphi) = 0, \tag{4}$$

$$\Phi(\varphi) = \theta_2(\varphi) \frac{\partial \varphi}{\partial t} - A \operatorname{div}[\theta_1(\varphi) \nabla\varphi] - H\Delta\left[\frac{\partial \theta_2(\varphi)}{\partial \varphi}(\nabla\varphi)^2 + \theta_2(\varphi) \Delta\varphi\right]. \tag{5}$$

For $\varepsilon = 0$ the equation $L(\varphi_0, 0) = 0$ is linearized. The constants B and C are found from the conditions (3) for $\varepsilon = 0$. This corresponds to an exponential approximation of the function φ ($\varphi = \varphi_S \exp[1/C(u-u_S)]$, in the first of conditions (3) and to its linear approximation $\varphi = \varphi_S + 1/B(u-u_S)$ in the second condition. Because of the contradiction in the conditions (3) at $\varepsilon = 0$, their mean values in the range of variation of u under consideration can be taken for B and C.

We seek the solution of (4) as a series in increasing powers of ε

$$\varphi(\varepsilon) = \varphi_0 + \sum_{m=1}^{\infty} \varepsilon^m \varphi_m, \quad m = 1, 2, 3, \ldots, \tag{6}$$

where the functions φ_0 and φ_m should be determined (φ_0 is the solution of the unperturbed equation (4) for $\varepsilon = 0$). Substituting $\varphi(\varepsilon)$ into (4) and grouping coefficients of identical powers in ε, we obtain the following infinite system of equations

$$B \frac{\partial \varphi_m}{\partial t} - AC \operatorname{div}(\nabla\varphi_m) + BH\Delta\Delta\varphi_m + \Phi_m = 0, \tag{7}$$

$$\Phi_m = \Phi_m(\varphi_0, \varphi_1, \ldots, \varphi_{m-1}) = \frac{1}{(m-1)!} \left(\frac{\partial^{m-1}\Phi}{\partial \varepsilon^{m-1}}\right)\bigg|_{\substack{\varphi=\varphi_0 \\ \varepsilon=0}}. \tag{8}$$

Since (4) is identical to the original equation (1) for $\varepsilon = 1$, we should put $\varphi(\varepsilon)$ in the solution $\varepsilon = 1$. The initial and boundary conditions are taken into account only to find φ_0 in the obtained series of boundary value problems. For $m = 1, 2, 3, \ldots$, they (containing the parameter ε in the zero power) become homogeneous. For this reason, taking account of the nonlinearities in the problem under consideration reduces, after its linearization, to taking account of the influence of the variable-intensity sources Φ_m in a system of boundary value problems of the same type.

Use of the perturbation method considered above for (1) is closely related to problems of bifurcation of the solutions of nonlinear equations [12]. The passage to a new unknown function φ hence permits making the difference $\varphi - \varphi_S$ less in comparison with $u - u_S$, and in turn this permits taking account of those perturbations $\Phi(\varphi)$ for which the perturbation parameter ε can be substantially different from zero and even equal to one. Since the errors of the exponential and linear approximations of the function φ emerge as perturbing functions with respect to which a perturbation theory series is constructed, the approach proposed then permits obtaining a solution as close as desired to the exact in the given range of $u - u_S$, in contrast to [11]. If the latter turns out to be too broad, resulting in degradation of the quality of the approximation of φ, then analogously to [11], it can be separated into several sub-integrals by then applying the same calculation scheme. Another approach to linearizing this problem and applying the perturbation method can be based on the results of [13].

The fundamental solution for the operator $L(\varphi_0, 0)$ is defined thus:

$$\Gamma(\mathbf{r}, \mathbf{r}', t-t') = L^{-1}\delta(\mathbf{r}-\mathbf{r}')\delta(t-t'), \tag{9}$$

where L^{-1} is the inverse operator to the original. It is easy to show that

$$\Gamma(\mathbf{r}, \mathbf{r}', t-t') = \frac{1}{(2\pi)^4} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \frac{\exp[i\mathbf{k}_1(\mathbf{r}-\mathbf{r}') + ik_2(t-t')] dk_1 dk_2}{Bik_2 - AC(ik_1)^2 + BH(ik_1)^4}. \tag{10}$$

The integral with respect to k_2 is here calculated by reliance on residue theory, and it is expedient to go over to a spherical coordinate system by directing the polar axis along the vector $\mathbf{R} = \mathbf{r} - \mathbf{r}'$ in order to integrate with respect to $\mathbf{k}_1$. Consequently

$$\Gamma(\mathbf{r}, \mathbf{r}', t-t') = \frac{\theta(t-t')}{2\pi^2 BR} \int_0^{\infty} \exp\left[\left(-\frac{AC}{B}k_1^2 - Hk_1^4\right)(t-t')\right] \sin(k_1 R) k_1 dk_1. \tag{11}$$

In the one-dimensional case

$$\Gamma(x, x', t-t') = \frac{\theta(t-t')}{\pi B} \int_0^\infty \exp\left[\left(-\frac{AC}{B}k_1^2 - Hk_2^4\right)(t-t')\right]\cos k_1(x-x')\,dk_1. \tag{12}$$

An exact calculation of (11) and (12) by using known functions is not apparently possible. Let I_1 and I_2 denote the integrals in (11) and (12), respectively, and in addition let $a = AC/B(t-t')$, $b = H(t-t')$. Let us make the change of variable $k_1^2 = y$ in I_1 and let us introduce the approximation $\sqrt{y} \approx \beta_1 y$, $\beta_1 = 1/\sqrt{y_0}$. The value of y_0 is selected in such a way that the interval $0-y_0$ turns out to be the essential domain of integration, i.e., so that $\sqrt{y_0} \gg \exp(-ay_0 - by_0^2)$. Hence

$$I_1 = \frac{i}{8}\sqrt{\frac{\pi}{b}}\,[\exp(\Psi_1^2)\,\mathrm{erfc}\,\Psi_1 - \exp(\Psi_2^2)\,\mathrm{erfc}\,\Psi_2],$$

$$\frac{a + iR\beta_1}{2\sqrt{b}} = \Psi_1, \quad \frac{a - iR\beta_1}{2\sqrt{b}} = \Psi_2, \quad \mathrm{erfc}\,\Psi_i = 1 - \Phi(\Psi_i), \tag{13}$$

where $\Phi(\Psi_i)$ is the probability integral. In order to emphasize the oscillatory nature of Γ, let us evaluate I_1 by another method by writing it as

$$I_1 = \frac{1}{2}\,\exp(b\alpha^2)\int_\alpha^\infty \exp(-by^2)\sin\left(R\sqrt{y-\alpha}\right)dy, \quad \alpha = \frac{a}{2b}. \tag{14}$$

Let us introduce the approximation $\sqrt{y-\alpha} \approx \beta_2(y-\alpha)$, $\beta_2 = 1/\sqrt{y_0 - \alpha}$ in the essential domain of integration, and let us represent I_1 as the difference between two integrals within the limits $0-\infty$ and $0-\alpha$. Evaluating the latter by using the theorem of the mean, we obtain that

$$I_1 = \frac{1}{2}\exp(b\alpha^2)\left\{\cos\gamma_1\left[\frac{\beta_2 R}{2b}\,\exp\left(-\frac{\beta_2^2 R^2}{4b}\right)\Phi\left(\frac{1}{2};\,\frac{3}{2};\,\frac{\beta_2^2 R^2}{4b}\right) - \frac{1}{\gamma_1\sqrt{b}}\,\Phi\left(\alpha\sqrt{b}\right)\left(1 - \cos\frac{\alpha}{\beta_2 R}\right)\right]\right.$$

$$\left. -\sin\gamma_1\left[\frac{1}{2}\sqrt{\frac{\pi}{\beta_2 R}}\,\exp\left(-\frac{\beta_2^2 R^2}{4b}\right) - \frac{1}{\gamma_1\sqrt{b}}\,\Phi\left(\alpha\sqrt{b}\right)\sin\frac{\alpha}{\beta_2 R}\right]\right\}, \quad \gamma_1 = \alpha\beta_2 R, \tag{15}$$

where $\Phi(c; d; x)$ is the degenerate hypergeometric function.

After making the change of variable $k_1^2 = y$ it is expedient to apply integration by parts to the integral I_2 and later introducing the approximation $\sqrt{y} \approx \beta_1 y$. Consequently

$$I_2 = \frac{i}{4n}\sqrt{\frac{\pi}{b}}\,[2\sqrt{b}\,\Psi_2\exp\left(-\Psi_2^2\right)\mathrm{erfc}\,\Psi_2 - 2\sqrt{b}\,\Psi_1\exp\left(-\Psi_1^2\right)\mathrm{erfc}\,\Psi_1$$

$$-a\exp\left(\Psi_2^2\right)\mathrm{erfc}\,\Psi_2 + a\exp\left(\Psi_1^2\right)\mathrm{erfc}\,\Psi_1], \quad n = x - x'. \tag{16}$$

The quantities Ψ_1 and Ψ_2 entering here are obtained from the expressions presented in (13) after R has been replaced by n. Just as (15) had been evaluated, it can be found that

$$I_2 = \frac{a - 2b\alpha}{n}\,I_1\Big|_{R=n} + \frac{2}{n}\,\exp(b\alpha^2)\left\{F_1\cos\gamma_2 - F_2\sin\gamma_2\right.$$

$$\left. -\frac{1 - \exp(-b\alpha^2)}{2\gamma_2}\left[\cos\gamma_2\left(1 - \cos\frac{\alpha}{n\beta_2}\right) - \sin\gamma_2\sin\frac{\alpha}{n\beta_2}\right]\right\}, \quad \gamma_2 = \alpha\beta_2 n, \tag{17}$$

$$F_1 = \frac{n\beta_2\sqrt{\pi}}{4\sqrt{b}}\,\exp\left(-\frac{n^2\beta_2^2}{4b}\right), \quad F_2 = \frac{1}{2} - \frac{n^2\beta_2^2}{4b}\Phi\left(1;\,\frac{3}{2};\,-\frac{n^2\beta_2^2}{4b}\right).$$

This expression for I_2 is more awkward than the preceding, however, it has the advantage that it does not contain the probability integral of imaginary argument. Asymptotic estimates for I_i can also be obtained by using the saddle-point method.

Only an approximate estimate of the expressions obtained for I_i is possible. The ratio ω between the areas under the line $\beta_1 y$ and the curve $\sqrt{y}$ within the limits $0-y_0$ or the ratio between the definite integrals with the functions $\sin R\beta_1 y$ and $\sin R\sqrt{y}$ between the same limits can be taken as this estimate. However, in the general case, the value of y_0 which depends on the unknown coefficients a and b, and therefore, on t, turns out to be unknown. (A rough estimate for the coefficient H is presented in [7] in one specific critical diffusion case.) The quality of the approximation $\sqrt{y} \approx \beta_1 y$ turns out to be higher, the smaller the interval $0-y_0$. The inaccuracy in the approximation will hence be felt principally in the nature

of the Green's function oscillations since $R\beta_1 y$ is the argument of the sine. It must be emphasized that the error in evaluating I_i can be reduced to practically zero by approximating $\sqrt{y}$ by lines in several intervals along y. It follows from a graph of the function $\sqrt{y}$ that an insignificant error is assured by two such intervals. (The results of these calculations are not presented since they turn out to be twice as long as those presented above.) Moreover, the accuracy of the calculations can be raised if I_i is multiplied by $1/\omega$.

Fundamental solutions, more convenient for the determination of the coefficient H by means of experimental results, can be obtained if a two-step approach to critical diffusion is used. For large deviations of the initial from the critical concentration, the rate of the diffusion processes in some time interval $t_0 - t$ is determined by the member with A in (1). The influence of the member with the coefficient H turns out to be dominant after the interval mentioned. This permits representing (1) as

$$\frac{du}{dt} = \theta(t_0 - t) A \operatorname{div}(u^2 \nabla u) - \theta(t - t_0) H \Delta \Delta u \tag{18}$$

and considering the influence of the members in the right side of (18) in turn. Consequently, for $t < t_0$ the form of the source $\Phi(\varphi)$ in the linearized equation is simplified, and its fundamental solution turns out to be analogous to the solution for the heat conduction equation. The integrals in the fundamental solutions for the equation with the linear term are a particular case of (11) and (12). The more complex integral in the one-dimensional solution is written in the tabulated form

$$I_3 = \frac{1}{2} \sqrt{\frac{\pi}{2n\beta_1}} \int_0^\infty \exp(-b_0 z^2) J_{-\frac{1}{2}}(z)\, dz, \quad b_0 = \frac{b}{n^2\beta_1^2}, \tag{19}$$

where $J_{-1/2}(z)$ is the Bessel function of the first kind. Hence

$$I_3 = \frac{1}{8} \sqrt{\frac{\pi}{\sqrt{b}}} \frac{\Gamma\left(\frac{1}{4}\right)}{\Gamma\left(\frac{1}{2}\right)} \exp\left(-\frac{1}{4b_0}\right) \Phi\left(\frac{5}{4};\ \frac{1}{2};\ \frac{1}{4b_0}\right). \tag{20}$$

Here $\Gamma(x)$ is the Euler gamma-function. The three-dimensional fundamental solution is also expressed in terms of the product of a negative exponential by a degenerate hypergeometric function. The time t_0 in (18) is determined just as has been done in [8].

According to [10], the Green's function G of the operator $L(\varphi_0, 0)$ in a domain D of arbitrary convex shape with a surface S, to each of whose elements the directions of the normal n at the boundary points $M, N, \ldots$ are defined, can be written as

$$G(r, r', t - t') = \Gamma(r, r', t - t') + \int_{t'}^t d\tau \iint_S q_n(r_M, r', \tau - t') \Gamma(r, r_M, t - \tau)\, d^2 r_M + \int_{t'}^t d\tau \iint_S q_n(r_M, r', \tau - t')\, d^2 r_M$$

$$\times \int_\tau^t d\xi \iint_S q_n(r_N, r_M, \xi - \tau) \Gamma(r, r_N, t - \xi)\, d^2 r_N + \cdots \tag{21}$$

In contrast to [10], a more complex expression than the Fourier law hence emerges as q_n:

$$q_n(r_M, r', \tau - t') = -\frac{AC}{B} \operatorname{grad}_{R_0} \left(\Gamma - \frac{HB}{AC} \Delta\Gamma\right) \cos(R_0, n),$$

$$R_0 = r_M - r'. \tag{22}$$

The Green's function $G = \Gamma + \Gamma_0$ for domains of classical shape can also be found if the Laplace transform is applied to the equation $L(\varphi_0, 0)\Gamma_0 = 0$ with homogeneous boundary conditions corresponding to the boundary value problem under consideration.

Using the well-known method from the theory of Green's functions of the many body problem [14], the integrals with respect to time, which are a convolution of functions, can be eliminated in (21) by subjecting G to a Fourier transform in the difference in time $t - t'$. Taking into account the fact that the contributions of the individual surface elements in the formation of G in the domain D turn out to be independent because of the superposition principle, it is easy to obtain a time-independent series for the Fourier transform

$$G(r, r', \omega) = \Gamma(r, r', \omega) + \iint_S q_n(r_M, r', \omega) \Gamma(r, r_M, \omega)\, d^2 r_M$$

$$+ \iint_S q_n(r_M, r', \omega)\, d^2 r_M \iint_S q_n(r_N, r_M, \omega) \Gamma(r, r_N, \omega)\, d^2 r_N + \cdots \tag{23}$$

After integrating over S while taking account of the real geometry of the domain D and summing the members of the series obtained by using the inverse Fourier transform, we find $G(r, r', t-t')$.

Let a stream of diffusing substance with the density $q(r_M, t)$ come into a part of the surface S_1 in the domain D, while this substance is absorbed with a stream density $Q(r_N, t)$ on the remaining part of the surface S_2, and moreover, sources of intensity $F(r, t)$ act within D. Then

$$\varphi_m(r, t) = \delta_n^0 \left\{ \int_0^t d\tau \left[\int\int_{S_1} q(r_M, \tau) G(r, r_M, t^*) d^2r_M - \int\int_{S_2} Q(r_N, \tau) G(r, r_N, t^*) d^2r_N + \int\int\int_D F(r', \tau) G(r, r', t^*) d^3r' \right] \right\}$$

$$+ \delta_m^n \int_0^t d\tau \int\int\int_D \Phi_m(r', \tau) G(r, r', t^*) d^3r', \quad t^* = t - t' - \tau, \quad n = 0, \ 1, \ 2, \ \ldots, \tag{24}$$

where δ_n^0 is the Kronecker delta.

Diffusion in some domain was considered above. If diffusion is analyzed in a capillary having a critical concentration at the initial instant, then the course of the diffusion will be reversible: first retarded, and then more rapid. Hence, the step functions in the members of (18) should interchange places. If the functions F, q, Q in (24) depended on u, then they should be transformed with respect to φ.

The recursion relationship (24) yields the solution of the formulated problem in quadratures. Let us examine some of its singularities. The deduction about the extremely slow progress of the critical diffusion processes, their non-monotoneity and oscillatory nature, made in [9], is verified by (13), (15)-(17), (20) which enter as cofactors in the expressions which can be considered sufficiently exact Green's functions of the operator L for an infinite space. It follows from these expressions that the velocity of the critical diffusion processes is determined, in contrast to the ordinary law $\sim \sqrt{2Dt}$, by the superposition of functions with more complex arguments. The oscillatory nature of the Green's function results in stratification of the concentration in the diffusion process in a spherically symmetrical manner around the source of substance. Taking into account the reflective properties of the walls, diffusion in a bounded space should be accompanied by effects recalling wave interference. Since the signs of the members in the Green's function turn out to be variable in time for a fixed point, then for some R the diffusion can, in principle, change sign in time, i.e., extraction can be observed instead of dissolution of the diffusing substance. Because of the strong retardation of the diffusion processes, the layers of substance turn out to be stable in time. A laminar configuration with weakly expressed transition domains is observed experimentally in the near-critical domain [6]. If such a configuration can actually be related to the behavior of the Green's function, then the possibility, in principle, arises in this case of determining the coefficient H experimentally by measuring the spacings between the individual gradient lines, or in other words, by means of the width of the layers. As the system temperature changes in the critical domain, the nature of the diffusion changes abruptly. The appearance of intensive convective currents and the formation of clearly expressed jets which then break up into individual drops [6] are possible. All this indicates the need for taking account of the terms describing the thermodiffusion pressure effect in (1).

Using the fundamental solutions obtained and the compensation principle formulated in [10], we can also solve the problem of critical diffusion even with more complex boundary conditions of the first kind.

NOTATION

c	is the concentration;
ε	is the perturbation parameter;
m	is the approximation;
r', t'	are the point radius-vector and the time of origination of a single source of substance;
r_M, r_N	are the radii vectors of the boundary points of the domain D.

Subscripts

s   denotes φ and u to the initial instant.

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