Kinetics of luminescence damping in the hopping mechanism of quenching

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A theory is developed of luminescence quenching in the presence of migration of the excitations over the donors. The kinetics of the luminescence damping is determined in the entire time scale. An expression is obtained for the rate of luminescence quenching for an arbitrary multipole interaction of the donors with the acceptors. It is shown that the Vavilov-Frank phenomenological theory is obtained from the theory developed in this paper, and the microscopic meaning of the parameters of the latter is explained. The microscopic meaning of the parameter Δ introduced earlier to explain the experimental data of Voron'ko *et al.* (Sov. Phys. JETP **44**, 251, 1976) is explained.

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The study of the migration of electronic excitation over impurities of the same kind is of interest both when it comes to ascertaining the physical nature of the interactions that lead to transfer of the energy of excitations, and for determining more accurately the generating characteristics of laser materials.

It was shown theoretically and experimentally in a preceding paper[1] that the data on excitation migration can be extracted directly from the time dependence of the luminescence. This deduction was based on a concept introduced in that reference, namely the hopping mechanism of luminescence quenching. The present paper is devoted to a development of the theory of the hopping mechanism of luminescence quenching, on the basis of a previously suggested model.[1,2] In this model, we consider a regular lattice of donors with an average distance $L = (3/4\pi n_D)^{1/3}$ between them, where n_D is the donor density in the sample. Although the actual arrangement of the donors in the sample is irregular, the principal role for excitation migration over the donors is played by the most probable configurations of the donors, and it is these which form a lattice with distance L between donors. In fact, analysis of a fluctuation in which two donors have turned out to be close to each other shows that the rapid smearing of the excitation over this pair gives grounds for regarding this pair as an excited dimer. On the other hand, further migration of the excitation from such a dimer to the remaining environment takes place within a time equal to the time of transfer of the excitation over the average distance L. The analysis of triple fluctuations and those of higher order is analogous. It is these considerations which justify this model.

The approach developed in the present paper, based on expansion in the parameter $n_A R_w^3 < 1$, where n_A is the acceptor density and R_w is the radius of the effective black sphere inside of which the excitations are certainly annihilated. As shown in the Appendix, the smallness of this parameter corresponds to the possibility of the condition $\Delta \tau_0 < 1$ of Burshtein's paper.[2] Smallness of the parameter $n_A R_w^3$ has made it possible to obtain an exact solution for the kinetics of luminescence quenching over the entire time scale. As to the temporal kinetics,

which was considered by Sakun,[3] it is valid only at $t/\tau_0 \ll 1$, where τ_0 is the time required to move the excitation over a distance L, and cannot be extrapolated to the times $t \gg \tau_0$ which are of greatest interest in experiment. In the subsequent analysis of the results of the present paper are advanced arguments that confirm this statement.

Within the framework of the aforementioned model, expressions are obtained for the quenching rate $\overline{W}_s$ for an arbitrary multipole interaction of donors with acceptors; these expressions agree with my earlier results.[4] An expression is obtained for the luminescence quantum yield in various limiting situations. It is shown that the Vavilov-Frank phenomenological theory[5] is obtained in natural fashion from the present theory. Criteria are obtained for the applicability of the Vavilov-Frank theory, and an interpretation of the microscopic meaning of the parameters of the latter is presented. An exact analysis of the kinetic yields an expression for the parameter Δ, which was empirically introduced by Voron'ko *et al.*[6] to account for the experimental data, and a microscopic interpretation of this parameter is given. A comparison with Burshteĭn's approach[2] is given in the Appendix.

The problem of the effect of donor and acceptor motion on the time dependence of luminescence damping was considered in a number of papers.[7–9] There is a certain similarity between the problems solved in these papers and our problem. There are, however, also substantial differences. The point is that excitation migration over donors that are contained in a solid matrix are not always described by a diffusion equation, so that it is necessary to solve the complete kinetic equation for the migration of the excitations over the donors.

We consider the quenching of the excitation by acceptors in the presence of excitation migration over the donors. Let the probability of hopping from a donor to an acceptor per unit time be $W(|\mathbf{r}|)$, where $|\mathbf{r}|$ is the distance between the donor on which the excitation is located and the acceptor. The main parameter that determines the physical picture of the quenching is R_w and determines the dimension of that region of space around

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the acceptor, within which the annihilation of the excitation is certain to take place. Accordingly, the parameter K_w can be estimated from the condition $W(R_w)\tau_0 \sim 1$, where τ_0 is the time of sojourn of the excitation within a sphere of radius R_w. Depending on the ratio of R_w to the average distance $L = (3/4\pi n_D)^{1/3}$ between the donors, where n_D is the donor density in the sample, the excitation can pass through the region of radius R_w via many hops—the quasidiffusion limit. This limiting case corresponds to the condition $L \ll R_w$ or as a result of a single hop—to the hopping mechanism of quenching.[1,2,4] This mechanism is realized under the condition $L \gg R_w$.

We confine ourselves in this paper to the hopping mechanism. In this case we can make some estimates even from simple physical considerations. If the probability of hopping from a donor to a donor is $K(r) = C_{DD}/r^3$, and the corresponding probability for donor–acceptor hopping is $W(r) = C_{DA}/r^m$, then the time of sojourn of the excitation inside a sphere of radius R_w is of the order of $\tau_0 \sim K(L)^{-1}$, $\tau_0 \sim C_{DD}^{-1} n_D^{-s/3}$. From this and from the condition $W(R_w)\tau_0 \sim 1$ we obtain an estimate for R_w:

$$R_w \sim (C_{DA}/C_{DD})^{1/m} n_D^{-s/3m}. \tag{1}$$

From the condition of the realization of the hopping mechanism we obtain a lower bound on the donors at $s > m$:

$$n_D \gg (C_{DA}/C_{DD})^{3/(s-m)} \tag{2}$$

and an inequality that serves as the upper bound of the donor density, at $s < m$:

$$n_D \ll (C_{DD}/C_{DA})^{3/(m-s)}. \tag{3}$$

When the multipolarities are equal, $s = m$, the condition for the realization of the hopping mechanism is independent of the donor density:

$$C_{DA} \ll C_{DD}. \tag{4}$$

It should be noted that at $s = m = 6$ the hopping mechanism has already been observed in neodymium compounds.[1,10] The case of higher multipolarities is possibly also realized in rare-earth compounds.[11-13]

In analogy with[10], we can obtain for the probability $m(t)$ that the excitation will not decay by the instant of time t the relation

$$m(t) = \exp\{-t/\tau_D - \varepsilon(t)\}, \tag{5}$$

$$\varepsilon(t) = \frac{n_A}{n_D} \sum_k [1 - f(r_k, t)], \tag{}$$

where the function $f(r, t)$ satisfies the equation

$$\frac{df(r, t)}{dt} = -W(r)f(r, t) - \frac{1}{\tau_0}f(r, t) + \sum_k K(r - r_k)f(r_k, t) \tag{6}$$

subject to the initial condition $f(r_k, 0) = 1$. Here τ_0 is the most probable donor–donor hopping rate, τ_D^{-1} is the proper rate of damping of the donor luminescence without the presence of acceptors. The summation is over the coordinates of the donors.

Formulas (5) and (6) are similar to the corresponding formulas of[9]. The difference lies in the more general equations satisfied by the function $f(r, t)$. From the relation (5), differentiating $\varepsilon(t)$ with respect to time and using (6), we obtain

$$\dot{\varepsilon}(t) = W(t) = n_A \int W(r) f(r, t) dr. \tag{7}$$

This relation is exceedingly useful, since the essential region in the integral (7), owing to the rapid decrease of $W(r)$ at large r, is of the order of R_w, thus showing that to obtain the instantaneous rate of luminescence quenching $W(t)$ it is necessary to know the exact behavior of the function $f(r, t)$ only in a region on the order of R_w around the acceptor.

We call attention to the fact that the third term in the right-hand side of (6) has the meaning of the flux to the point r from outside of R_w, i.e., from distances on the order of $L \gg R_w$, where the perturbing effect of absorption by an acceptor does not manifest itself, since the flux is independent of time. As a result, Eq. (6) reduces to

$$\frac{df(r, t)}{dt} = -W(r)f(r, t) - \frac{1}{\tau_0}f(r, t) + Y \tag{8}$$

under the condition $f(r, 0) = 1$, where

$$Y = \sum_k K(r - r_k)f^s(r_k), \tag{9}$$

and $f^s(r)$ is the stationary solution of Eq. (6). The solution of (8) is

$$f(r, t) = f^s(r) + [1 - f^s(r)]\exp\{-[W(r) + \tau_0^{-1}]t\}, \tag{10}$$

$$\tau_0 = \sum_k K(r - r_k). \tag{}$$

We write down the equation for $f^s(r)$ in a form more useful for future use

$$f^s = \frac{Y}{W(r) + \tau_0^{-1}}. \tag{11}$$

The function $f^s(r)$ has a characteristic dimension R_w, and at $r \gg R_w$ we have $f^s(r) = 1$. Since the summation in (9) is over distances on the order of L and larger, and since $L \gg R_w$, we get accurate to terms of the order of $n_D R_w^3 \ll 1$

$$Y = \sum_k K(r - r_k) = \frac{1}{\tau_0}. \tag{12}$$

Substituting (12) in (11), using (10) and (7), and carrying the corresponding integrations, we obtain for the instantaneous luminescence quenching rate

$$W(t) = \frac{1}{\tau_0} \int_0^t Q(\tau) \exp\left(-\frac{\tau}{\tau_0}\right) d\tau + Q(t)\exp\left(-\frac{t}{\tau_0}\right), \tag{13}$$

$$Q(\tau) = n_A \int dr\{1 - \exp[-\tau W(r)]\}. \tag{14}$$

Formulas (13) and (14) settle the question of the kinetics of luminescence quenching.

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At $t \gg \tau_0$ it is easy to obtain an asymptotic formula for the quenching rate:

$$W_s = \frac{1}{\tau_0} \int_0^\infty \dot{Q}(\tau) \exp\left(-\frac{\tau}{\tau_0}\right) d\tau. \qquad (15)$$

Formula (15) was first obtained in[11] for the donor-acceptor dipole interaction. This formula has a simple physical interpretation. The quantity $\dot{Q}(\tau)$ has the meaning of the instantaneous rate of the Förster decay. At large times, when mixing of the excitations takes place, the quenching proceeds at a rate $\dot{Q}(\tau)$ within the time of sojurn τ of the excitation in a sphere of radius R_w. Since the sojourn times are subject to a scatter with a Poisson distribution, the resultant quenching rate is obtained by averaging $\dot{Q}(\tau)$ over this time scatter.

For multipole interaction, expressions (13) and (14) yield

$$\varepsilon(t) = \left[\frac{t}{\tau_0} + 1 - \frac{3}{m}\right] \frac{3}{m} Q(\tau_0) \gamma\left(\frac{3}{m}, \frac{t}{\tau_0}\right) + \frac{3}{m} Q(t) \exp\left(-\frac{t}{\tau_0}\right), \qquad (16)$$

where

$$\gamma(l, x) = \int_0^x z^{l-1} e^{-z} dz$$

is the incomplete gamma-function,[14] $Q(t)$ satisfies the relation

$$Q(t) = \alpha t^{3/m}, \qquad (17)$$

and α is given by the formula

$$\alpha = {}^4/_3 \pi n_A \Gamma(1 - 3/m) C_{DA}^{3/m}, \qquad (18)$$

where n_A is the density of the acceptors in the sample and $\Gamma(x)$ is the Euler gamma function.[14] If the donor-acceptor interaction is dipole-dipole, then putting $m = 6$ in (16) we readily obtain

$$\varepsilon(t) = \frac{2\pi^2}{3} n_A (C_{DA}\tau_0)^{1/2} \left[\frac{1}{2} \Phi\left(\left(\frac{t}{\tau_0}\right)^{1/2}\right)\right.$$
$$\left. + \frac{t}{\tau_0} \Phi\left(\left(\frac{t}{\tau_0}\right)^{1/2}\right) + \exp\left(-\frac{t}{\tau_0}\right)\left(\frac{t}{\pi\tau_0}\right)^{1/2}\right]. \qquad (19)$$

Here

$$\Phi(x) = \frac{2}{\pi^{1/2}} \int_0^x e^{-z^2} dz$$

is the probability integral.[14]

From (16) and (5) we readily obtain the asymptotic behavior of the kinetics of the luminescence damping at times much longer than the time τ_0 of a single hop:

$$m(t) = \exp[-t/\tau_D - \overline{W}_s t - \Delta], \qquad (20)$$

where

$$\overline{W}_s = \Gamma(3/m + 1) Q(\tau_0)/\tau_0, \qquad (21)$$

and Δ satisfies the following relation:

$$\Delta = (1 - 3/m) Q(\tau_0) \Gamma(3/m + 1). \qquad (22)$$

At $t \ll \tau_0$ expressions (16), (17), and (5) yield for the damping kinetics the relation

$$m(t) = \exp\left\{-\frac{t}{\tau_D} - \alpha t^{3/m} - \frac{\alpha}{\tau_0} t^{3/m+1} \frac{1 - 3/m}{1 + 3/m}\right\}. \qquad (23)$$

The second term in the exponential describes the well known Förster law of luminescence quenching. The third term describes the correction to the Förster law for the presence of excitation migration over the donors.

As already mentioned in the interaction, the damping kinetics obtained by Sakun[3] must be interpreted in the same spirit. Thus, the formal expansion in the donor density n_D used in[3] is in effect an expansion in the small parameter $n_D(C_{DD}t)^{3/s} = (t/\tau_0)^{3/s}$. Therefore the second term in Sakun's formula is none other than a small correction to the Förster law of luminescence damping, necessitated by the presence of excitation migration over the donors. It should be noted that this correction, as obtained in the present paper, has a somewhat different time dependence than the analogous correction in Sakun's paper.[3] The apparent cause of this difference is that Sakun considered a random distribution of the donors. It is precisely the unsubstantiated extrapolation of this correction to times $t \gg \tau_0$ which led to Sakun's statement[3] that the kinetics of the quenching process is not exponential at large times $t \gg \tau_0$ if the multipolarity of the interaction is higher than dipole-dipole. As shown earlier,[4] at times $t \gg \tau_0$ the quenching process always becomes exponential. The asymptotic quenching rate $\overline{W}_s$, however, as seen from the results in[4], is not analytic in the donor density n_D, and therefore this result cannot be obtained by expansion in powers of n_D, as proposed by Sakun.[3] The same conclusion is reached also by an analysis of the diagrams not accounted for on[3], which are divergent. We note that the result obtained for $\overline{W}_s$ in[4] was repeated in a later study.[15]

Although in the case of dipole-dipole interaction the already mentioned correction obtained by Sakun[3] for the Förster law depends on t linearly and on C_{DA}, C_{DD}, n_D, and n_A in the same manner as $\overline{W}_s$, this correction cannot be identified with $\overline{W}_s$ by virtue of the already mentioned restriction $t \ll \tau_0$. The numerical coefficients in this correction and of $\overline{W}_s$ are, as expected, different. Therefore the agreement between the dependences of this correction and $\overline{W}_s$ on the parameters must be regarded as fortuitous and connected with the dimensionality relation. It should be noted that the luminescence-damping character described by (20) was observed in experiment.[6]

Formula (22) reveals the microscopic meaning of the parameter Δ. In fact, it is easily seen that

$$\Delta = {}^4/_3 \pi n_A R_w^3 (1 - 3/m), \qquad (24)$$

where R_w is the radius of the effective black sphere inside which the quenching is certain to take place. R_w^3 satisfies the relation

$$R_w^3 = \Gamma(3/m + 1) \Gamma(1 - 3/m) (C_{DA}\tau_0)^{3/m}. \qquad (25)$$

Therefore the factor $e^{-\Delta}$ in (20) has the meaning of the number of acceptors that do not fall in the instantaneous quenching volume, which was first introduced phenomenologically in quenching theory by Vavilov.

Formula (21) also has a simple physical meaning, which manifests itself most clearly when a somewhat different form is used for (21):

$$\overline{W}_s = {}^1\!/_3 \pi n_A R_w^3 / \tau_0. \tag{26}$$

Formula (26) has the meaning of the number excitations that move at a frequency $1/\tau_0$ and land in a unit time in the volume of the effective black sphere.

Since the experiment is frequently performed with stationary illumination of the sample and the measured quantity is the luminescence quantum yield (LQY), it is of interest to obtain the LQY within the framework of the hopping mechanism of quenching. The correct expression for the LQY η is

$$\eta = \frac{1}{\tau_D} \int_0^\infty \exp\left[-\frac{t}{\tau_D} - \varepsilon(t) \right] dt. \tag{27}$$

The behavior of the LQY as defined by formula (27) and by (16) and (17) is different in the three limiting situations a), b), and c), which differ from one another by the different relations between the parameters $n_A R_w^3$ and τ_D/τ_0.

Situation a) corresponds to two cases:

$$1) \tau_D/\tau_0 \ll 1, \quad n_A R_w^3 (\tau_D/\tau_0)^{3/m} \ll 1,$$
$$2) \; \tau_D/\tau_0 \ll 1, \quad (n_A R_w^3)^{m/3} \gg 1, \tag{28}$$

In case 1), expanding $\varepsilon(t)$ under the integral sign in (27) in powers of $1/\tau_0$, and also in powers of $Q(\tau_D)$, we obtain for the LQY the expression

$$\eta = 1 - Q(\tau_D)\Gamma\left(\frac{3}{m}+1\right) - Q(\tau_D)\frac{m-3}{m}\Gamma\left(\frac{3}{m}+1\right)\frac{\tau_D}{\tau_0}. \tag{29}$$

In case 2), just as in 1), expanding $\varepsilon(t)$ in powers of $1/\tau_0$, we obtain for the LQY the formula

$$\eta = \eta_0 \left[1 - \frac{\Gamma(2m/3+1)}{\Gamma(m/3)Q^{m/3}(\tau_0)}\frac{m-3}{m+3} \right], \tag{30}$$

where η_0 is the LQY in the case when there is no migration, and is given by

$$\eta_0 = \Gamma\left(\frac{m}{3}+1\right) Q^{-m/3}(\tau_D). \tag{31}$$

The situation b) corresponds to the following two conditions:

$$\tau_D/\tau_0 \gg 1, \quad n_A R_w^3 < 1. \tag{32}$$

In this situation, the proper damping time of the luminescence is much longer than the time τ_0 of a single hop. Therefore, taking the second condition into account, the LQY is determined by the asymptotic kinetics (20) at $t \gg \tau_0$:

$$\eta = \frac{e^{-\Delta}}{1+\overline{W}_s\tau_D}. \tag{33}$$

Expression (33) for the LQY is the known formula of the Vavilov-Frank phenomenological theory,[5] where, however, formulas (21) and (22) explain the microscopic meaning of the phenomenological parameters Δ and $\overline{W}_s$ and yield the connection between these parameters and the most probable time τ_0 of one hop, and also with the parameter C_{DA} that characterizes the force of the interaction of the donor with the acceptor.

The remaining situation c) is realized under two conditions:

$$n_A R_w^3 \ll 1, \quad n_A R_w^3 \tau_D/\tau_0 \ll 1. \tag{34}$$

We note that in situation c) the relation between τ_D and τ_0 can be arbitrary. In this situation, expanding the exponential under the integral sign in (27) in powers of $\varepsilon(t)$, we obtain

$$\eta = 1 - \frac{Q(\tau_D)}{(1+\tau_D/\tau_0)^{3/m-1}}\Gamma\left(\frac{3}{m}+1\right). \tag{35}$$

Formulas (29), (30), (33), and (35) settle the question of the LQY. We note in conclusion that these formulas show that the LQY depends substantially on the donor-donor hopping time τ_0. By measuring the LQY we can therefore obtain τ_0, and accordingly the parameter C_{DD} that characterize the donor-donor interaction force.

APPENDIX

As an Appendix we compare the approach of[2] with the present approach and obtain a general expression for the LQY at arbitrary ratios of the parameters. In[2] the value of $m(t)$ satisfies the integral relation

$$m(t) = N(t)\exp\left(-\frac{t}{\tau_0}\right) + \frac{1}{\tau_0}\int_0^\infty m(t-\tau)N(\tau)\exp\left(-\frac{\tau}{\tau_0}\right)d\tau, \tag{36}$$

where $N(t)$ describes the quasistatic decay without allowance for migration, and is equal to

$$N(t) = e^{-Q(t)}. \tag{37}$$

Taking the Laplace transform of (36), we get

$$m(t) = \frac{1}{2\pi i}\int_{a-i\infty}^{a+i\infty} dp\, e^{pt} \frac{Y(p+\tau_0^{-1})}{1-\tau_0^{-1}Y(p+\tau_0^{-1})}, \tag{38}$$

$$Y(p+\tau_0^{-1}) = \int_0^\infty \exp[-(p+\tau_0^{-1})\tau]N(\tau)d\tau. \tag{39}$$

We take the logarithm of (36) and expand the quantity $\varepsilon(t) = -\ln m(t)$ in powers of the density n_A. Confining ourselves to the first-order approximation, we get

$$\varepsilon(t) = \frac{1}{2\pi i}\int_{a-i\infty}^{a+i\infty} dp\, e^{pt} \frac{(p+\tau_0^{-1})^2}{p^2} \cdot$$
$$\int_0^\infty d\tau \exp\left[-\left(p+\frac{1}{\tau_0}\right)\tau\right]Q(\tau). \tag{40}$$

Changing the order of the integration and evaluating the integrals, we obtain for $\varepsilon(t)$ the relation

$$\varepsilon(t) = \tau_0^{-1}\int_0^t (t-\tau)Q(\tau)\exp\left(-\frac{\tau}{\tau_0}\right)d\tau + \int_0^t Q(\tau)\exp\left(-\frac{\tau}{\tau_0}\right)d\tau. \tag{41}$$

Differentiating (41) with respect to time, we obtain (13), thus demonstrating the equivalence of the two approaches.

In conclusion, we derive a general formula for the LQY. We note for this purpose that the general definition of the LQY is none other than the Laplace transform of the function $m(t) = e^{-\varepsilon(t)}$, where $p = \tau_D^{-1}$. Therefore, using (38), we obtain for the LQY the general expression

$$\eta = \frac{Y(\tau_D^{-1} + \tau_0^{-1})}{1 - \tau_0^{-1} Y(\tau_D^{-1} + \tau_0^{-1})}. \tag{42}$$

In the case of a donor—acceptor dipole-dipole interaction we have $m = 6$ and the formulas (42), (39) and (17) yield for the LQY the relation

$$\eta = \frac{Y(\tau'^{-1})}{1 - \tau_0^{-1} Y(\tau'^{-1})}, \quad \tau' = \frac{\tau_D \tau_0}{\tau_D + \tau_0}, \tag{43}$$

while $Y(\tau')$ is given by

$$Y(\tau'^{-1}) = \tau' \left[1 - \frac{\alpha}{2} (\tau' \pi)^{1/2} \exp\left(\frac{\alpha^2 \tau'}{4}\right) \operatorname{erf}\left(\frac{\alpha \tau'^{1/2}}{2}\right) \right], \tag{44}$$

where $\operatorname{erf}(x) = 1 - \Phi(x)$, and $\Phi(x)$ is the error integral.[14]

We note that Watts[16] solved the equations of[2] by numerical methods.

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Diffusion near the critical point under conditions of large concentration gradients

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Binary diffusion in a capillary is computed by a perturbation theory method for the case when the mutual-diffusion coefficient and the solution density depend on the concentration. The calculation is in agreement with experiments performed on diffusion in a CO_2–Ar solution near the critical point for vaporization of CO_2. It is shown that, at low Ar concentrations, the obtained experimental dependence of the mutual-diffusion coefficient on the reduced temperature τ can be described with satisfactory accuracy for values of τ up to 10^{-4}–10^{-5} by a theory in which the Onsager coefficient (mobility) is regular.

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Systematic experimental investigations on diffusion near the critical point, which have established a strong slowing down of the concentration relaxation processes, were begun in the fifties by Krichevskii and his co-workers.[1] An explanation of this slowing down was given by Leontovich within the framework of the self-consistent field theory for the case when the particle mobility is regular at the critical point.[2]

The application of laser techniques to the measurement of Rayleigh line widths at the end of the sixties made it possible[3] (see also Swinney and Cummin's review article[4]) to come close to the critical point without significantly perturbing the system and to discover a new competing diffusion mechanism. An interpretation of these results has been given in a number of papers[3–7] on the basis of the theory of interacting modes and the scaling-law hypothesis. The main result of this interpretation, in so far as the problem of interest to us here is concerned, is that, in a region sufficiently close to the critical point, the mutual-diffusion coefficient D_{12} can be represented thus:

$$D_{12} = L^s (\partial \mu / \partial C)_{p, T} + L^r (\partial \mu / \partial C)_{p, T}, \tag{1}$$

where L^s and L^r are the singular and regular parts of

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