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Quenching by Static Traps: Initial-Value and Steady-State Problems

Marshall Fixman
Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523
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Simulations and effective-medium calculations were performed on the absorption of impurity particles by static sinks in three dimensions. The theory shows no qualitative effects due to two-sink clusters and agrees well with simulations. The conclusion is drawn that effective-medium theory is adequate for time-dependent impurity concentrations $C(t)$ above the lower bound recently demonstrated by several authors. Crossing of the concentration curves occurs at a time such that $C(t)/C(0) = 10^{-67}$ or less.

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The conventional theory of diffusion-controlled reactions, such as impurity quenching in metals, exciton trapping, or enzyme catalysis, is based on an effective-medium theory (EMT) that may be traced to Smoluchowski.[1-3] The concentration $C(t)$ of the diffusing species decays through absorption by sinks, which are here taken to be fixed in position. For three-dimensional systems $C(t)$ shows asymptotically exponential time dependence.[4] In contrast, the asymptotic result $\ln[C(t)/C(0)] \propto -t^{3/5}$ has been shown to be exact[5-10] for a Poisson distribution of perfectly absorbing sinks, in the limit of large systems. The proof that the nonexponential decay is a lower bound has been generalized to nonoverlapping and partially absorbing sinks.[8] The proof is based on the occurrence of arbitrarily large regions devoid of sinks. I consider the conditions under which EMT needs to be supplemented by consideration of such voids.

Balagurov and Vaks[5] supposed that EMT would be adequate for times less than the t_x at which the computed $C(t)$ dropped below the lower bound. However, this criterion needs to be supported by evidence that EMT does not break down, because of large fluctuations in sink density, long before the crossing point. I supply such evidence in the form of a comparison between two levels of approximation in EMT, and computer simulations. The second level of approximation, EMT2, accounts for clusters of two sinks. Clustering effects are omitted in EMT1. It is found that EMT2 gives a significant quantitative improvement over EMT1 at high sink concentrations, but gives no qualitative change. Moreover, the effect of pairs of sinks separated by more than a few diameters is quite negligible, which indicates that large-scale density fluctuations will not introduce a new time scale that signals the breakdown of EMT in low-order approximations. This is in agreement with the scaling arguments of Tokuyama and Cukier.[11] Accepting then the criterion of Balagurov and Vaks[5] and supplying the numbers they omitted, we find that EMT should be adequate for $C(t)/C(0)$ below[4] its value 10^{-67} at the crossing point for perfectly absorbing and nonoverlapping[8] spherical sinks at a volume fraction $v_f = 0.1$. Still lower values are found at higher or lower concentrations, or for imperfectly absorbing spheres.

Similar estimates for two-dimensional systems lead to a maximum value $C(t_x)/C(0) = 10^{-21}$ at the surface fraction $v_f = 0.1$. However, I supply no evidence that low-order EMT converges in two

dimensions. It is quite possible that the failure of EMT will be gradual in two dimensions, and will be seen at still shorter times, because of the greater strength of long-wavelength density fluctuations in two dimensions compared to three.

I introduce some notation necessary for a summary of the calculations. Let $c(\vec{k},s)$ be the Laplace and Fourier transform of the mean impurity concentration $C(\vec{r},t)$ with respect to $\exp(-st+i\vec{k}\cdot\vec{r})$. $c(\vec{k},s)$ is the linear response of the impurity concentration, averaged over sink distributions, to an external driving source $w(\vec{k},s)$. $w(\vec{k},s)$ is the transform of some $W(\vec{r},t)$, and $W(\vec{r},t)$ and $C(\vec{r},t)$ are assumed to vanish for $t<0$. An initial-value problem is obtained if $W(\vec{r},t)$ has a $\delta(t)$ factor, and a steady-state problem results if $W(\vec{r},t)$ has a time-independent part for $t>0$. (Steady-state calculations will be reported as incidental evidence concerning EMT; however, the main focus is on the initial-value problem.) The linear response may be written

$$sc=-k^2c-\gamma(k,s)c+w. \tag{1}$$

The unit of length is taken to be the radius a of the spherical sinks, and the unit of time is a^2/D, where D is the diffusion constant. The self-energy $\gamma(s)\equiv\gamma(0,s)$ is closely related to the mean flux into one sink.

The simulations were carried out in terms of a microscopic impurity concentration $P(\vec{r},t)$. We have $C(\vec{r},t)=\langle P(\vec{r},t)\rangle$, where $\langle\cdots\rangle$ is an average over the spatial distribution of sinks. For I spherical sinks of radius a centered at $\vec{R}_i$, we take

$$\frac{\partial P}{\partial t}=\nabla^2P-\sum K_i(t)\epsilon(\vec{r}-\vec{R}_i)+W(\vec{r},t), \tag{2}$$

$$K_i(t)=\lambda\int\alpha(\vec{r}-\vec{R}_i)P(\vec{r},t)d^3r. \tag{3}$$

$\alpha(r)$ and $\epsilon(r)$ are prescribed functions that vanish for $r>a$. λ is a rate parameter and $K_i(t)$ is the total flux into sink i. For the specific results to be discussed, α and ϵ were $1/v$ for $r<a$, where v is the sink volume. Equation (2) was Laplace transformed and solved for the transforms $k_i(s)$ of $K_i(t)$, with spatial boundary conditions that are discussed below. Inverse Laplace transformation was carried out numerically. The only random feature in the simulation is the sink distribution. This procedure, described in more detail elsewhere,[12] is advantageous at low sink concentrations or for continuum models in comparison to a direct simulation of diffusing particles.[13] The average of $k_i(s)$ over sinks and sink configurations is $\gamma c/\rho$, where $\rho=v_f/v$ is the sink concentration.

The sinks were enclosed within a spherical surface of radius R, on which boundary conditions were imposed. For the results reported here the surface was open to an external medium characterized by a self-energy $\gamma_{ex}(s)$, except that the total flux through the surface was required to vanish as it does for periodic boundary conditions. Standard techniques allow the boundary conditions to be satisfied to specified order l_{mx} in a spherical harmonic expansion. $\gamma_{ex}(s)$ was calculated in the coherent-potential approximation,[14] which is a standard version of EMT, to the lowest order EMT1. Incorporation into the boundary conditions of the improved version EMT2 discussed below made no significant difference in the simulation results. Several recent contributions[15-17] to the quenching problem, expressed variously in the languages of multiple scattering or EMT, seem to embody notions similar to those of the coherent-potential approximation.

In the lowest approximation EMT1, the diffusion equation has to be solved for just a single sink in the effective medium. In the next approximation EMT2 the equation has to be solved for two spheres at arbitrary separation $R_{12}>2a$ in the effective medium. This problem was solved for the fluxes $k_1(R_{12},s)$ and $k_2=k_1$ to arbitrarily high accuracy with use of a Schwinger variational approach. $k_i(R_{12},s)$ is about 15%–20% lower at $R_{12}=2a$ than at large R_{12}, for small s and small ρ. The variation is less for large s and ρ. It turned out that corrections to EMT1 deriving from large R_{12}, more than 3 sink radii, were quite negligible. Essentially the whole correction of EMT2 over EMT1, indeed all the correction in the approximation used here, resulted not from the variation of $k_1(R_{12},s)$, but from the requirement of nonoverlapping sinks. [The neglect of variation in $k_1(R_{12},s)$, here approximated by $k_i(\infty,s)$, was estimated to cause errors of up to 10% in the correction that EMT2 makes to EMT1 for steady-state problems, and up to 30% of the correction for initial-value problems.]

I report results first for the steady state, where $W=W_S$ is independent of $\vec{r}$ and of t for $t>0$. With L_S defined by $\rho K_S=W_S=\rho C_S L_S$, Table I gives L_S for the simulations and for EMT1 and EMT2, for various volume fractions. The simulation results were obtained on systems of 256 sinks, with boundary conditions satisfied through $l_{mx}=5$. I used $\lambda=40$. This value corresponds to a steady-state rate $L_S=\lambda/(1+0.3\lambda/\pi)=8.299$ at $v_f=0$, which is about 0.66 of the rate 4π for perfectly absorbing, impenetrable spheres. Convergence with respect to I and l_{mx} was estimated to be reached to

TABLE I. Steady-state and initial-value results. The second-order steady-state rate constant L_S is given for several volume fractions v_f. Rate parameter $\lambda = 40$. Simulation results are under the heading SIM, and coherent-potential approximations under EMT1 and EMT2. The simulation results were obtained on systems of 256 spherical sinks, with boundary conditions satisfied through $l_{mx} = 5$. $C(t_x)/C(0)$ is the fraction of impurity particles remaining at the crossing time t_x such that the effective-medium calculation of $C(t_x)$ drops below the known lower bound. The sinks are perfectly absorbing and nonoverlapping.

	L_S			
v_f	SIM	EMT1	EMT2	$C(t_x)/C(0)$
0	· · ·	8.299	8.299	0
0.001	8.56	8.55	8.55	10^{-442}
0.01	9.20	9.14	9.20	10^{-145}
0.05	10.93	10.41	10.91	10^{-77}
0.1	12.80	11.59	12.81	10^{-67}
0.2	16.69	13.71	16.72	10^{-75}

within a few tenths of a percent, and statistical uncertainties seemed comparable. (The uncertainties in rates for the initial-value simulation were considerably larger, up to several percent at the higher densities and longer times.)

Results for the initial-value problem are shown in Fig. 1 in terms of the effective rate $R(t)$, where

$$C(t) = C(0)\exp[-\rho R(t)t]. \quad (4)$$

Note that the time scale T in Fig. 1 is reversed and distorted from t, in order to allow compression of the data. The vertical ticks provide values of $C(t)/C(0)$. Numerical inversion of Laplace transforms is inherently an ill-conditioned problem, and we were not able to carry $C(t)/C(0)$ below 10^{-4} to 10^{-5} with 8-byte arithmetic. However, $R(t)$ shows virtually straight-line dependence on T through some four decades drop in $C(t)/C(0)$, either for the simulations or for EMT1 and EMT2. It seems probable that the downward curvature to $R(\infty) = 0$ required by the existence of a nonexponential lower bound would be found, if at all, only in very high-order EMT approximations. We assume, then, that the linear dependence of $R(t)$ on T will proceed to larger times until t is so large that absorption at the boundaries of large voids provides a faster channel for decay.[5]

According to Kayser and Hubbard,[8] generalization of the Grassberger-Procaccia lower bound[6] to

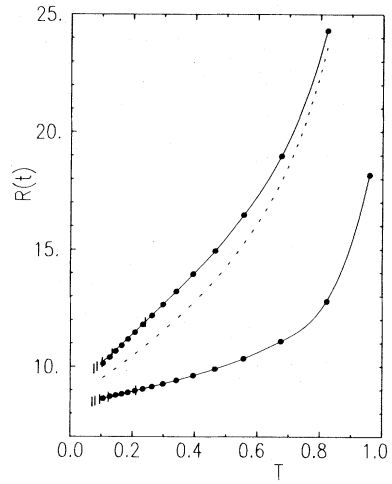

FIG. 1. Apparent second-order rate constant $R(t)$ vs T for the initial-value problem. $T = (1+20v_f t)^{-1/2}$. $R(0) = \lambda = 40$. The upper curves are for $v_f = 0.1$ and give $R(t)$ for the coherent-potential approximations EMT2 (solid) and EMT1 (dashed). The lower curve (solid) gives the EMT2 results for $v_f = 0.01$. The points give corresponding results obtained from the simulation of 256 spherical sinks with boundary conditions satisfied through $l_{mx} = 5$. The five vertical ticks on each solid curve denote interpolated and extrapolated points for which $C(t)/C(0) = 10^{-n}$, $n = 9$ (left), 7, 5, 3, and 1 (right).

partially absorbing sinks with an arbitrary rather than Poisson distribution requires only the substitution of $p/k_B T$ for ρ, where p is the pressure exerted by the sinks. Moreover, the time t_x at which the EMT $C(t)$ crosses the lower bound is rather large, and the value of $R(t_x)$ from EMT will be near its apparent limiting value, say R^*; see Fig. 1. Crossing then occurs at

$$\rho R^* t_x = v_3^{3/2}(p/\rho k_B T)(R^{*3/2}\rho^{1/2})^{-1}, \quad (5)$$

where $v_3 = 13.73$ is the constant calculated by Grassberger and Procaccia.[6] The pressure on the right-hand side of (5) was estimated from the Percus-Yevick compressibility formula,[18] and R^* was replaced by 4π, an approximate long-time value for perfectly absorbing spheres. Corresponding values of $C(t_x)/C(0)$ are shown in Table I for a range of sink concentrations. It seems reasonable to conclude that the effective-medium approach is adequate for conventional three-dimensional quenching problems.

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[1]M. V. Smoluchowski, Phys. Z. 17, 557, 585 (1916).

[2]U. M. Gösele, "Reaction Kinetics and Diffusion in Condensed Matter," Habilitationsschrift, Universitat Stuttgart, 1983 (unpublished).

[3]T. R. Waite, Phys. Rev. 107, 463 (1957).

[4]EMT shows nonexponential transients in any number of dimensions. In one and two dimensions these transients persist and make $\ln[C(t)/C(0)]$ asymptotically proportional to $-t^{1/2}$ or $-t/\ln t$, respectively, in the lowest-order EMT. See Ref. 2. Suppression of the transients leads to short-time limits [B. Ya. Balagurov and V. G. Vaks, Zh. Eksp. Teor. Fiz. 65, 1939 (1973) [Sov. Phys. JETP 38, 968 (1974)]] on EMT, which are of no concern here.

[5]Balagurov and Vaks, Ref. 4.

[6]P. Grassberger and I. Procaccia, J. Chem. Phys. 77, 6281 (1982).

[7]R. F. Kayser and J. B. Hubbard, Phys. Rev. Lett. 51, 79 (1983).

[8]R. F. Kayser and J. B. Hubbard, to be published.

[9]F. Delyon and B. Souillard, Phys. Rev. Lett. 51, 1720 (1983).

[10]M. D. Donsker and S. R. S. Varadhan, Comments Pure Appl. Math. 28, 525 (1975), and 32, 721 (1979).

[11]M. Tokuyama and R. I. Cukier, J. Chem. Phys. 76, 6202 (1982).

[12]M. Fixman, Phys. Rev. B 15, 5741 (1977).

[13]G. Zumofen and A. Blumen, Chem. Phys. Lett. 88, 63 (1982).

[14]R. J. Elliott, J. A. Krumhansl, and P. L. Leath, Rev. Mod. Phys. 46, 465 (1974).

[15]M. Muthukumar, J. Chem. Phys. 76, 2667 (1982).

[16]B. U. Felderhof, J. M. Deutch, and U. M. Titulaer, J. Chem. Phys. 76, 4178 (1982).

[17]R. I. Cukier and K. F. Freed, J. Chem. Phys. 78, 2573 (1983).

[18]D. A. McQuarrie, *Statistical Mechanics* (Harper and Row, New York, 1976).