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Disorder-induced anomalous kinetics in the $A+A\rightarrow 0$ reaction

Jeong-Man Park[1,2] and Michael W. Deem[1]
[1]*Chemical Engineering Department, University of California, Los Angeles, California 90095-1592*
[2]*Department of Physics, The Catholic University, Seoul, Korea*

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We address the two-dimensional bimolecular annihilation reaction $A+A\rightarrow 0$ in the presence of random impurities. Impurities with sufficiently long-ranged interactions are known to lead to anomalous diffusion, $\langle r^2(t)\rangle \sim t^{1-\delta}$, in the absence of reaction. Applying renormalization group theory to a field theoretic description of this reaction, we find that this disorder also leads to anomalous kinetics in the long time limit: $c(t) \sim t^{\delta-1}$. This kinetics results because the disorder forces the system into the (sub)diffusion controlled regime, in which the kinetics must become anomalous. [S1063-651X(98)06503-9]

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Surface reactions show a variety of complex spatial and temporal patterns. Simple systems, such as oxidation of CO on single crystal Pt(110), show surprisingly rich behavior [1], ranging from spirals and standing waves to chemical turbulence [2,3]. Such behavior results because two dimensions is the upper critical dimension for many surface reactions, and so collective fluctuations control the dynamics. Toussaint and Wilczek and Kang and Redner first noticed the diffusion-controlled kinetics that can arise from reactant microphase separation [4–6]. Field theoretic techniques were developed that rigorously showed two dimensions to be the upper critical dimension for the annihilation reactions $A+A\rightarrow 0$ [7,8] and $A+B\rightarrow 0$ [9]. Adsorption effects have been addressed within the field theoretic framework [10]. Real systems, of course, possess many defects, and randomness in adsorption energies can lead to a variety of phases observed at steady state [11].

Defects can dramatically affect the diffusion of particles if correlations in the potential field are sufficiently long ranged. For a single ion diffusing in disorder that is charged, the appropriate form of the correlation function at long wavelengths is [12]

$$\hat{\chi}_{vv}(k)=\gamma/k^2. \tag{1}$$

For this model, the upper critical dimension is 2. In two dimensions and below, subdiffusion occurs [13,14]. In this anomalous regime the mean-square displacement increases sublinearly with time, $\langle r^2(t)\rangle \sim t^{1-\delta}$. The diffusion exponent, $1-\delta$, depends on the strength of disorder; it can be found exactly [15–21].

These same defects can have an effect on reacting species. We consider species that diffuse in this quenched, random potential and which also react according to the law $A+A\rightarrow 0$. The diffusing species, however, do not interact in any other way.

The type of physical system that we have in mind is a reaction that occurs on the surface of a crystalline ionic lattice. The substrate lattice has dislocation line pairs, which form line vacancies or line interstitials. These defects are immobile and generate a random, quenched electrostatic potential on the surface, represented by Eq. (1). On the surface, the reaction $A+A\rightarrow 0$ occurs, where A is a reactive ion. The $1/r$ interaction between the ions is technically irrelevant, and so it can be ignored. So as to maintain surface charge neutrality, however, we may wish to include additional counter ions, which can desorb.

Alternatively, our results can be viewed as approximately describing the annealing of two-dimensional topological defects, such as line dislocations in solids. Topological defects have logarithmic interactions, due to a slowly decaying elastic strain field (see [22] for a review). If some of the defects were pinned and unreactive, the remaining defects would diffuse and combine in the quenched, random potential described by Eq. (1). The logarithmic interaction between the topological defects prevents microphase separation, and so the kinetics of this two-species reaction is similar to that of the $A+A$ reaction [4].

In this paper we analyze a field theoretic formulation of the two-dimensional annihilation reaction $A+A\rightarrow 0$ in the presence of quenched disorder. The concentration of A is initially Poissonian, with average density n_0. No creation or unimolecular annihilation is allowed. We search for the asymptotic decay law at long times using renormalization group (RG) theory. A field theory is derived by identifying a master equation, writing the master equation in terms of creation and annihilation operators, and using the coherent state representation [7,8]. The random potential is incorporated with the replica trick [14]. The concentration of A at time t, $c(\mathbf{x},t)$, is given by

$$c(\mathbf{x},t)=\lim_{N\rightarrow 0}\langle a(\mathbf{x},t)\rangle , \tag{2}$$

where the average is taken with respect to $\exp(-S)$, with the action $S=S_0+S_1+S_2+S_3$,

$$S_0=\int d^d\mathbf{x}\int_0^{t_f}dt\,\bar{a}_\alpha(\mathbf{x},t)[\partial_t-D\nabla^2+\delta(t)]a_\alpha(\mathbf{x},t),$$

$$S_1=\int d^d\mathbf{x}\int_0^{t_f}dt[\lambda_1\bar{a}_\alpha(\mathbf{x},t)a_\alpha^2(\mathbf{x},t)+\lambda_2\bar{a}_\alpha^2(\mathbf{x},t)a_\alpha^2(\mathbf{x},t)],$$

$$S_2=-n_0\int d^d\mathbf{x}\bar{a}_\alpha(\mathbf{x},0),$$

$$S_3=\frac{\beta^2D^2}{2}\int dt_1dt_2\int_{\mathbf{k}_1\mathbf{k}_2\mathbf{k}_3\mathbf{k}_4}(2\pi)^d\delta(\mathbf{k}_1+\mathbf{k}_2+\mathbf{k}_3+\mathbf{k}_4)$$
$$\times\hat{\bar{a}}_{\alpha_1}(\mathbf{k}_1,t_1)\hat{a}_{\alpha_1}(\mathbf{k}_2,t_1)\hat{\bar{a}}_{\alpha_2}(\mathbf{k}_3,t_2)\hat{a}_{\alpha_2}(\mathbf{k}_4,t_2)$$
$$\times\mathbf{k}_1\cdot(\mathbf{k}_1+\mathbf{k}_2)\mathbf{k}_3\cdot(\mathbf{k}_1+\mathbf{k}_2)\hat{\chi}_{vv}(|\mathbf{k}_1+\mathbf{k}_2|). \tag{3}$$

Summation is implied over replica indices. The notation $\int_{\mathbf{k}}$ stands for $\int d^d\mathbf{k}/(2\pi)^d$. The upper time limit in the action is arbitrary as long as $t_f\geqslant t$. The term S_0 represents simple diffusion, without an external potential. The δ function, often left out by convention, enforces the initial condition on the free field propagator. The term S_1 comes from the reaction terms. The parameters are related to the conventional reaction rate, k, by $\lambda_1=2\lambda_2=k$. The term S_2 comes from the random, Poissonian initial condition. The term S_3 comes from averaging the concentration over the random potential. The potential is assumed to be Gaussian, with zero mean and correlation function given by Eq. (1). The inverse temperature is given by $\beta=1/(k_\mathrm{B}T)$.

An approximate solution to Eq. (2) can be derived by a saddle point approximation to the action (3). The result, before the average over the random potential is taken, is

$$\partial_t c_v=D\nabla^2c_v+\beta D\boldsymbol{\nabla}\cdot(c_v\boldsymbol{\nabla}v)-\lambda_1c_v^2,$$
$$c_v(\mathbf{x},0)=n_0. \tag{4}$$

For constant potential, this equation has the solution $c_v(\mathbf{x},t)=1/(\lambda_1t+1/n_0)$.

An alternative, exact expression for the concentration can be derived by performing a Hubbard-Stratonovich transformation on Eq. (3) and integrating out the field $\bar{a}$:

$$\partial_t c_{\eta v}=D\nabla^2c_{\eta v}+\beta D\boldsymbol{\nabla}\cdot(c_{\eta v}\boldsymbol{\nabla}v)-\lambda_1c_{\eta v}^2+i\eta c_{\eta v},$$
$$c_{\eta v}(\mathbf{x},0)=n_0, \tag{5}$$

where the real, Gaussian, random field η has zero mean and variance $\langle\eta(\mathbf{x},t)\eta(\mathbf{x}',t')\rangle=2\lambda_2\delta(\mathbf{x}-\mathbf{x}')\delta(t-t')$. The physical concentration is given by averaging the solution over the random field η. From this representation, we see that mean field theory is exact when $\lambda_2 = 0$. It is for this reason that diagrams to all orders in λ_1 can be summed in this limit (see, for example, [8]).

We apply renormalization group theory to the action (3) to take into account the effects of nonzero λ_2. Time ordering prevents a term of the form $\bar{a}\bar{a}$ from being generated, and all other relevant terms are already present in Eq. (3). The limit $N\rightarrow 0$ turns out not to matter, as time ordering cancels the same terms that this limit does. We follow the flow equations until λ_2 is small enough so that we have entered the perturbative regime. In this regime, we can match the flow equations with the solution to Eq. (4). We integrate over momenta in the range $\Lambda/b<k<\Lambda$ and then rescale the fields by $\hat{\bar{a}}'(b\mathbf{k},b^{-z}t)=\hat{\bar{a}}(\mathbf{k},t)/\bar{\alpha}$ and $\hat{a}'(b\mathbf{k},b^{-z}t)=\hat{a}(\mathbf{k},t)/\alpha$. To achieve a fixed point, and to keep the time derivative in S_0 constant, we set $\alpha=1,\bar{\alpha}=b^d$. We determine the dynamical exponent by requiring that the diffusion coefficient remain unchanged. The flow equations in two dimensions, to one loop order, then become

$$\frac{d\ln n_0}{dl}=2,$$

$$\frac{d\ln\lambda_1}{dl}=-\frac{\lambda_2}{2\pi D}+\frac{3\beta^2\gamma}{4\pi},$$

$$\frac{d\ln\lambda_2}{dl}=-\frac{\lambda_2}{2\pi D}+\frac{3\beta^2\gamma}{4\pi},$$

$$\frac{d\beta^2\gamma}{dl}=0. \tag{6}$$

The dynamical exponent is given by

$$z=2+\frac{\beta^2\gamma}{4\pi}\ . \tag{7}$$

These flow equations reproduce known anomalous scaling in the cases of no reaction or no disorder. They are integrated to a time such that

$$t(l^*)=te^{-\int_0^{l^*}z(l)dl}=t_0\ . \tag{8}$$

The matching time, t_0, is chosen to be on the order of $4\pi^2/(\Lambda^2D)$ so as to be within the range of validity of both RG scaling and mean field theory. Mean field theory is a good approximation at this time because $\lambda_2(l^*)$ is small. (An expansion in λ_2 generates an expansion in t_0 that leads to subdominant scaling.) For short times, particles see only the local value of the potential, and the effective diffusivity is given by the bare value. (An expansion in β generates an expansion in t_0 that leads to subdominant scaling.) We can, therefore, ignore the potential term in Eq. (4) for short times. Matching with mean field theory, we find the mean square displacement is given by

$$\langle r^2(t(l^*),l^*)\rangle=4Dt(l^*) \tag{9}$$

in the absence of reaction, and the concentration profile is given by

$$c(t(l^*),l^*)=\frac{1}{1/n_0(l^*)+\lambda_1(l^*)t(l^*)} \tag{10}$$

in the absence of random forces. The observed values are related by scaling:

$$\langle r^2(t)\rangle = e^{2l}\langle r^2(t(l),l)\rangle,$$
$$c(t)=e^{-2l}c(t(l),l). \tag{11}$$

With no reaction, the one-loop flow equations prove to be exact [15–21]. The disorder strength is not renormalized to any order. The dynamical exponent is greater than 2, and so we have subdiffusive behavior. Matching at $l=l^*$, we find the mean square displacement at long times is given by

$$\langle r^2(t)\rangle \sim 4Dt\left(\frac{t}{t_0}\right)^{-\delta}, \tag{12}$$

with

$$\delta=\left[1+\frac{8\pi}{\beta^2\gamma}\right]^{-1}. \tag{13}$$

We have a continuously variable exponent that depends on the strength of disorder. The prefactor is nonuniversal, since the matching time t_0 explicitly enters.

With no external potential, the flow equations become asymptotically exact at long times [7,8]. The rate constants decay slowly to zero, with the ratio $\lambda_2(l)/\lambda_1(l)$ remaining constant. The dynamical exponent is 2, since there is no field renormalization. Matching with mean field theory at $l=l^*$, we find for long times

$$c(t)\sim\frac{\ln(t/t_0)}{8\pi Dt}. \tag{14}$$

We see the characteristic universal logarithmic correction to the mean-field kinetic equations. There is a subdominant, nonuniversal $1/t$ decay.

The presense of disorder dramatically affects the reaction. The rate constants no longer decay to zero, but to a nonzero fixed point. The ratio $\lambda_2(l)/\lambda_1(l)$ again remains constant. To one loop, we find the reaction terms do not renormalize the diffusivity, disorder strength, or dynamical exponent. Matching with mean field theory at $l=l^*$, we find

$$c(t)\sim\frac{1}{\lambda_1^* t}\left(\frac{t}{t_0}\right)^{\delta}, \tag{15}$$

with the fixed point given from Eq. (6) as

$$\lambda_1^*=3D\beta^2\gamma. \tag{16}$$

We have, therefore, a nonuniversal decay exponent that depends, again, on the strength of disorder. The exponent is precisely the inverse of that for the pure diffusion case, Eq. (12). The prefactor is also nonuniversal, since the matching time t_0 again enters.

We see that to one loop, the reaction terms leave the diffusion process unaffected. Physically, the disorder traps diffusing species in wells of deep potential energy. Normal diffusion between these wells leads to the observed, overall diffusivity. Progressively deeper wells are encountered at longer times, and so anomalous diffusion occurs. For diffusion limited reactions, the effective reaction rate is proportional to the effective diffusion constant. Since we have $D_{\text{eff}}(t)\sim D(t/t_0)^{-\delta}$, we should expect $k_{\text{eff}}\propto(t/t_0)^{-\delta}$. This is exactly the behavior observed in Eq. (15).

When two reactants are attracted to the same well, reaction almost always occurs, since the escape time is much greater than the reaction time. In other words, the reaction becomes (sub)diffusion limited, and the bare reaction rate should not enter the decay law. Three species entering a well is much less probable at low densities than two, and so this case should be irrelevant at long times. Reactants can encounter each other outside the wells. Reaction outside the wells would show up as renormalization of the disorder strength and dynamical exponent in a two-loop calculation. We have checked that these terms are not generated to two-loop order. So the dynamical exponent is unchanged by the reaction, and the bare reaction rate is not present in the decay law. From this argument, we expect the dynamical exponent and the flow equation for the disorder to remain unchanged in higher order calculations.

The diffusion terms, on the other hand, do affect the reaction process. Since the reaction becomes diffusion limited, the diffusion terms actually control the reaction process. For this reason, we find a nonzero fixed point for the effective reaction rate. The effective reaction rate should be a function of the strength of disorder, since it is related to the rate at which species diffuse between wells. The rate (at $l=l^*$) is proportional to the effective diffusion coefficient divided by a characteristic distance squared. This is exactly the behavior that we observe in Eq. (16), with $\beta^2\gamma$ an inverse distance squared. Higher order calculations may, of course, lead to modification of the numerical value of the fixed point for large $\beta^2\gamma$.

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[1] M. Graham *et al.*, Science **264**, 80 (1994).

[2] M. Eiswirth and G. Ertl, in *Chemical Waves and Patterns*, edited by R. Kapral and K. Showalter (Kluwer, Dordrecht, 1995).

[3] S. Jakubith *et al.*, Phys. Rev. Lett. **65**, 3013 (1990).

[4] D. Toussaint and F. Wilczek, J. Chem. Phys. **78**, 2642 (1983).

[5] K. Kang and S. Redner, Phys. Rev. Lett. **52**, 955 (1984).

[6] K. Kang and S. Redner, Phys. Rev. A **30**, 2833 (1984).

[7] L. Peliti, J. Phys. A **19**, L365 (1986).

[8] B. P. Lee, J. Phys. A **27**, 2633 (1994).

[9] B. P. Lee and J. Cardy, J. Stat. Phys. **80**, 971 (1995); **87**, 951 (1997).

[10] M. Droz and L. Sasvaári, Phys. Rev. E **48**, R2343 (1993).

[11] L. Frachebourg, P. L. Krapivsky, and S. Redner, Phys. Rev. Lett. **75**, 2891 (1995).

[12] M. W. Deem and D. Chandler, J. Stat. Phys. **76**, 911 (1994).

[13] D. S. Fisher *et al.*, Phys. Rev. A **31**, 3841 (1985).

[14] V. E. Kravtsov, I. V. Lerner, and V. I. Yudson, J. Phys. A **18**, L703 (1985).

[15] V. E. Kravtsov, I. V. Lerner, and V. I. Yudson, Phys. Lett. A **119**, 203 (1986).

[16] J. P. Bouchaud, A. Comtet, A. Georges, and P. L. Doussal, J. Phys. (France) **48**, 1445 (1987).

[17] J. P. Bouchaud, A. Comtet, A. Georges, and P. L. Doussal, J. Phys. (France) **49**, 369 (1988).

[18] J. Honkonen, Y. M. Pis'mak, and A. V. Vasil'ev, J. Phys. A **21**, L835 (1988).

[19] J. Honkonen and Y. M. Pis'mak, J. Phys. A **22**, L899 (1989).

[20] S. É. Derkachov, J. Honkonen, and Y. M. Pis'mak, J. Phys. A **23**, L735 (1990).

[21] S. É. Derkachov, J. Honkonen, and Y. M. Pis'mak, J. Phys. A **23**, 5563 (1990).

[22] D. R. Nelson, in *Phase Transitions and Critical Phenomena*, edited by C. Domb and J. Lebowitz (Academic Press, New York, 1983), Vol. 7.