Scaling theory of particle annihilation in systems with a long-range interaction

Valeriy V. Ginzburg, Paul D. Beale, and Noel A. Clark
Condensed Matter Laboratory, Department of Physics, University of Colorado, Boulder, Colorado 80309-0390
(Received 13 February 1995)

A scaling theory is presented which takes into account the influence of long-range power-law interactions on the density decay rate in a system of charged particles which move in a viscous medium and annihilate via the bimolecular reaction $A_+ + A_- \rightarrow 0$. Various regimes of the annihilation process depending on system dimensionality d and long-range-force power exponent n, are discovered and analyzed.

PACS number(s): 05.60.+w, 61.72.Cc, 66.10.Cb, 82.20.Db

In recent years, the problem of particle annihilation via reaction of the type $A_+ + A_- \rightarrow 0$ in systems with or without long-range forces acting between the particles has been studied intensely because of wide range of its possible applications (astrophysics, plasma physics, chemical kinetics, solid state physics, etc. [1–4]). The case with no long-range interactions present has become well known after Toussaint and Wilczek [3] suggested that particle density ρ decays with time as $t^{-d/4}$, due to the growth of one-species domains that slows annihilation and yields an anomalous dimension for the density field. This effect vanishes in four dimensions, where fluctuations become weak and crossover occurs to the mean-field behavior, characterized by particle density decay as t^{-1}, as expected for a bimolecular reaction (see, e.g., [5]). (Note that for a one-species annihilation problem, $A + A \rightarrow 0$, no anomalous dimension arises and $\rho \propto t^{-d/2}$ with crossover to mean field at $d = 2$, as expected from pure dimensional analysis. We will not discuss this case here anymore.) Computer simulations have been carried out for the reaction $A_+ + A_- \rightarrow 0$ [6], mostly confirming the general results of Toussaint and Wilczek.

The case with long-range interactions is of interest mostly because of its connection with XY-model kinetics, in which field singularities can be treated as particles. In the two-dimensional XY system, vortices and antivortices interact via $(1/r)$ force. Several computer simulations of such systems, recently carried out, showed that annihilation of these singularities exhibits a rather nontrivial dynamics [7]. In our recent work [8], the annihilation of point defects in freely suspended liquid crystal films was simulated and a scaling theory was proposed to explain strong deviations from the mean-field equation $\rho(t) \propto t^{-1}$. Following the ideas of Mondello and Goldenfeld [9], we considered the role of initial fluctuations in the annihilation kinetics and showed that in a two-dimensional system with charged particles interacting via $1/r$ force, particle number density decays with time as $t^{-6/7}$. In this paper, we develop a scaling theory for systems of arbitrary dimensionality d and long-range force power exponent n and show that the role of initial fluctuations is rather unique in the $d = 2$, $n = 1$ case (discussed in [8]). We also investigate the range of validity of the mean-field theory for different d and n and find critical points in (d,n) space, where mean-field exponents coincide with scaling predictions.

We consider a d-dimensional system consisting of particles of negative $(-q)$ and positive $(+q)$ charges, interacting via the pairwise force

$$F_{12} = \frac{q_1 q_2}{R^n} , \tag{1}$$

where R is the interparticle distance. The system as a whole has zero total charge, which means that the average density of positive particles, ρ_+, is always equal to the average density of negative particles, ρ_-. Of course, at any given moment there are subregions with excess of positive particles or negative particles.

We will consider only systems with $2 \le d \le 4$ for reasons that will be explained later. The phase space (d,n) is shown in Fig. 1, where points I, II, and III correspond to Toussaint-Wilczek systems with integer d; point IV corresponds to $d = 2$, $n = 1$.

We define as a special class of systems the "Gaussian" systems, which satisfy the condition $n = d - 1$. For such systems, the Gauss theorem holds, meaning that in any selected domain of (large enough) size L, equilibrium charge density fluctuation is given by (for details see [8,9])

$$\delta\rho(L) = \frac{\delta N}{c_d L^d} \cong \frac{(\rho_0 d_0 L^{d-1})^{1/2}}{L^d} \cong \rho_0 (L/d_0)^{-(d+1)/2} , \tag{2}$$

where $c_d = \pi, 4\pi/3$ for $d = 2,3$ and for spherical region; $d_0 = (\rho_0)^{1/d}$ is the characteristic length at time $t = 0$.

Another remarkable class of systems is that with no long-range interaction: particles interact only by annihilating when they come within distance r_0 from each other. In this case, fluctuations of particle number are proportional to $\sqrt{N}$, and density fluctuations are therefore given by

$$\delta\rho(L) = \frac{\delta N}{c_d L^d} \cong \frac{(\rho_0 L^d)^{1/2}}{L^d} \cong \rho_0 (L/d_0)^{-(d/2)} . \tag{3}$$

We can expect, obviously, that for all systems between these two extreme cases (i.e., with $d - 1 < n < +\infty$), particle number of fluctuations change from one limit to

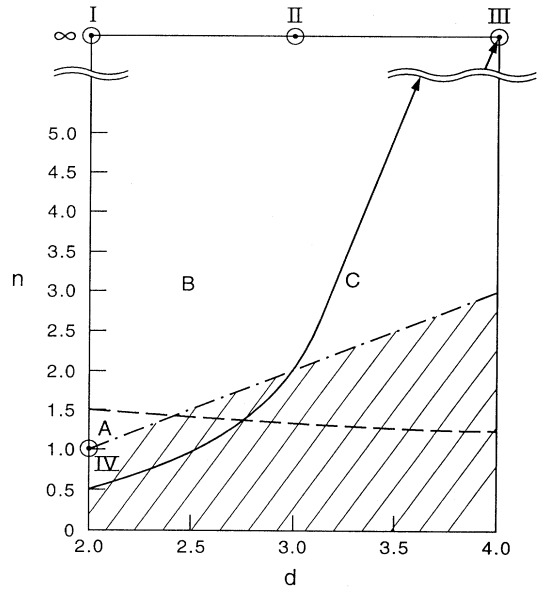

FIG. 1. Phase diagram in (d,n) plane. Lettered regions correspond to A—"Anomalous" region: $\rho \propto t^{-\nu}$, $\nu<1$, $\langle R^2\rangle \propto t^{1+\varepsilon}$, $\varepsilon>0$; B—"Diffusive" region: $\rho \propto t^{-\nu}$, $\nu<1$, $\langle R^2\rangle \propto t$; C—"Kinetic-rate or mean-field" region: $\rho \propto t^{-1}$, $\langle R^2\rangle \propto t$. Roman numerals correspond to systems for which numerical simulations have been done. The dashed line is the border between diffusion (above) and superdiffusion (below) systems; the dashed-dotted line is the line of Gaussian systems—the region below this line corresponds to unphysical cases; the solid line is the border between slow fluctuation-limited annihilation (left) and quick mean-field annihilation (right).

another as n grows. Therefore, for all systems with $d \geq 2$, $n \geq 1$, we assume

$$\delta\rho(L) \cong \rho_0 (L/d_0)^{-\mu} , \tag{4}$$

where $\mu(n,d)$ is taken to be a linear function of d and $(1/n)$, satisfying both borderline cases (linear interpolation):

$$\mu(n,d) = \frac{d}{2} + \frac{d-1}{2n} . \tag{5}$$

Now, let us consider particle dynamics. Motion of an ith particle is described by the Langevin equation:

$$\eta \frac{d\mathbf{R}_i}{dt} + m\frac{d^2\mathbf{R}_i}{dt^2} = \sum_j \frac{q_i q_j}{|\mathbf{R}_i - \mathbf{R}_j|^{n+1}} (\mathbf{R}_i - \mathbf{R}_j) + \mathbf{f}_i(t) , \tag{6}$$

where η is the inverse mobility, m is the particle mass, the j summation is over all pair interactions, and $\mathbf{f}_i(t)$ is a thermal random force. Two terms on the right-hand side of Eq. (6) are the forces driving deterministic and diffusion components of particle motion in the system.

In the absence of large-scale fluctuations, particles would move only diffusively; even though random forces from neighbors would influence the motion of a particle, they would only rescale the diffusion constant and have no effect on the annihilation exponents. Still, in order to note this rescaling, we will use the notation D' instead of D, meaning that both thermal and interaction random forces are included.

Large-scale density fluctuations change this picture dramatically. In the system, there exist regions with net positive charge and regions with net negative charge. We will again see the enhanced diffusivity described in the previous paragraph, but now some of the particles (predominantly those that initially happened to be in regions with nonzero net charge) will travel large distances before annihilation, and their motion will be more Lagrangian than Brownian. We would say these particles constitute the mobile part of the system, while the other ones, that initially were in neutral regions, constitute the immobile part of the system [10]. Then, we can formulate two principles governing annihilation kinetics:

(i) The trajectory of mobile particles is determined mainly by the density of other mobile particles, not by the density of immobile particles.

(ii) The particle density decay is determined by the slower of the following two processes: travel of mobile particles between net-charged regions and annihilation of immobile particles in neutral regions. If the second process is slower, mean-field behavior with annihilation exponent 1 is observed, otherwise different fluctuation-produced exponents can appear.

Let us now compare these two processes for an arbitrary system, denoted by a point (d,n) in two-dimensional phase space.

Immobile particles obey the standard kinetic equation:

$$\frac{d\rho_i}{dt} = -K g_{+-}(r_0,t)\rho_i^2 , \tag{7}$$

where $g_{+-}(r,t)$ is a pair correlation function for particles with opposite charges, ρ_i is the density of immobile particles, and K is the reaction rate constant.

If we set $g(r,t)=1$ (neglecting fluctuations), we obtain the well-known mean-field result (for large t)

$$\rho_i \cong (Kt)^{-1} . \tag{8}$$

Annihilation of mobile particles is fully determined by their displacements. Since at the beginning they found themselves surrounded by particles of the same charge, they need to travel to the nearest cluster of particles of opposite sign before annihilation. We suppose that mobile particles can start annihilating when their displacement becomes comparable to L, defining a time t_L.

On the other hand, for each L, the density of mobile particles is given by Eq. (4). This allows us to state that at time t_L, the density of mobile particles is $\delta\rho(L)$ [as defined in Eq. (4)], and the displacement of each mobile particle is of the order of L. To describe the mobile particle density decay, therefore, we need to establish the exact dependence of t_L on L, or vice versa. To do this, we

transform equation of motion (6) by multiplying both parts by $\mathbf{R}_i$ and ensemble-averaging it over all mobile particles (see, e.g., [11]):

$$\frac{dR^2}{dt}=2dD'+\frac{\langle \mathbf{F}*\mathbf{R}\rangle}{\eta} . \tag{9}$$

We assume that force acts in general along the trajectory, so the second term on the right-hand side is nonzero and can be estimated as

$$\langle \mathbf{F}*\mathbf{R}\rangle \equiv q^2[\rho(L)]^{-(n/d)}L , \tag{10}$$

while on the left-hand side, $R^2 \cong L^2$. After substituting $\rho(L)$ from Eq. (4), we obtain for the t dependence of L:

$$\frac{dL^2}{dt}=2dD'+(q^2/\eta)\rho_0^{(n/d)}d_0^{\alpha}L^{1-\alpha} , \tag{11}$$

where $\alpha=n\mu$.

The system of Eqs. (4), (5), and (11) describes the decay rate for the density of mobile particles. It is important to notice that this system is valid only for $L \gg d_0$. In this limit, from Eq. (11) one can obtain $L(t)$, and thereby $t_L(L)$, so that L becomes a parameter mapping initial density fluctuation $\delta\rho(L)$ to the density ρ at time t_L. By solving Eq. (11), therefore, we obtain a scaling law of particle density decay.

We now analyze some possibilities for the dependence of annihilation kinetics on d and n. First, in order to have the nondiffusion contribution to mobile particle motion prevail, the power of L on the right-hand side of Eq. (11) ought to be positive. If this is not the case, the forces between mobile particles are weak and at the later stage of the annihilation process cannot compete with diffusion; mobile particles drift in the system in almost the same way as the immobile ones. This leads us to the requirement that $1-\alpha>0$. Systems that satisfy this condition lie below the dashed line in Fig. 1. For those systems, we can disregard diffusion terms when integrating Eq. (11) to obtain

$$L \cong d_0^{\tau}(q^2t/\eta)^{\kappa} , \tag{12}$$

$$\rho \cong d_0^{\sigma}(q^2t/\eta)^{-\nu} , \tag{13}$$

where $\tau=(\mu-n)/(1+\alpha)$, $\kappa=1/(1+\alpha)$, $\sigma=(\alpha-d)-\alpha(\mu-n)/(1+\alpha)$, and $\nu=\mu/(1+\alpha)$. Thus, for the $d=2$, $n=1$ case, corresponding to defect interaction in two-dimensional systems, we obtain $\nu=6/7\approx 0.85$, $\kappa=4/7\approx 0.57$. Since the mean-field exponents are $\nu=1$, $\kappa=0.5$, we find that for such a system, large-scale fluctuations slow down annihilation, even though mobile particles travel faster than diffusion. As we will see, for two-dimensional systems, long-range fluctuations always slow down the annihilation very significantly.

All other physically interesting cases correspond to points in the (d,n) plant that lie above the dashed line in Fig. 1. In those cases, interaction between mobile particles is not strong enough to compete with random forces, and mean-square displacement of mobile particles becomes the same as that of immobile ones: $L^2 \cong 2dD't$, while the time dependence of the mobile particle density now becomes

$$\rho \cong d_0^{\sigma}(D't)^{-\nu} , \tag{14}$$

where $\sigma=\mu-d$, $\nu=(\mu/2)$.

According to postulate (ii) above, if the density decay is to be determined by mobile particle annihilation, this process has to be slower than bulk annihilation, and therefore, ν has to be less than 1. This inequality divides the (d,n) plane into two parts as shown in Fig. 1 with a solid line, and for all systems with $n \le (d-1)/(4-d)$ the mean-field description of the annihilation process is correct. It can be seen that for all systems with $d \ge 4$, mean-field theory always can describe the kinetics of particle annihilation reasonably well. For the case $d=2$, the mean-field description never works for physically interesting systems. For the borderline case $d=3$, the mean-field description is correct for the case $n=2$ (ionic solution, Coulomb forces), but fails for all other cases.

To sum up, we calculate decay exponents for several integer d's and n's and compare them with experimental or computational data (see Table I).

For $d=2$, $n=1$, comparison is made with our own simulation results [8]; for $d=2$, $n=\infty$, comparison is made also with our simulation results, as well as with simulations and theoretical calculations by Toussaint and Wilczek [3] and Kang and Redner [2]; for $d=3$, $n=\infty$, results of numerical simulation of Leyvraz [12], as well as theoretical predictions of Kang and Redner and Lebowitz and Bramson [13] were used for comparison.

For $d=2$, $n=1$, we also measured mean-square displacement of particles as a function of time and found that at large times, particles indeed move quicker than expected in pure diffusive systems. In Fig. 2 (reprinted from [8] with modifications), the "expected pair annihilation time" t_e (quantity proportional to the square of the initial distance between two annihilating particles R^2) is plotted in double logarithmic coordinates versus the actual time of the annihilation t_a. The slope of the curve changes from 1 at short times (diffusive behavior) to approximately 1.14 at long times (superdiffusive behavior). Within the accuracy of the simulation, measured exponent 1.14 ± 0.05 is in perfect agreement with the predicted value $\kappa=\frac{8}{7}\approx 1.143$.

The proposed scaling theory is the first attempt thus far to include arbitrary power-law long-range interactions of charged particles in the annihilation picture. It was known for some time that for $d<4$, diffusion, rather than the reaction kinetics itself, determines long-time density decay. We showed here that inclusion of long-range interactions speeds up annihilation process significantly by two mechanisms: suppression of initial charge density

TABLE I. Exponents ν for the density decay, $\rho(t) \propto t^{-\nu}$, for different d,n.

d \ n	1	2	3	∞
2	0.84 (0.85–0.9)	0.625	0.58	0.50 (0.5–0.55)
3		1.0	0.92	0.75 (0.75)
4			1.0	1.0

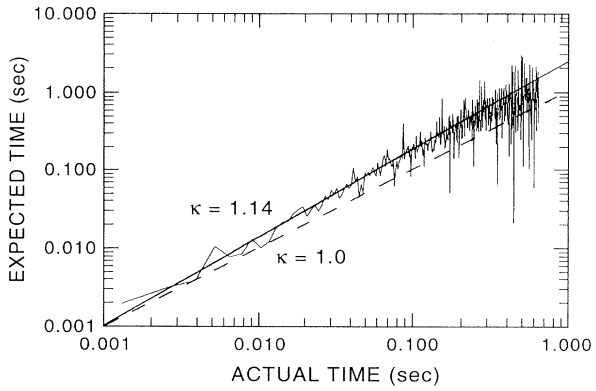

FIG. 2. "Expected annihilation time" vs actual annihilation time for a simulated system with $d=2$, $n=1$. "Expected annihilation time" is the time required for the chosen pair to annihilate in the absence of other charged particles and is proportional to the square of the initial distance between annihilating particles, with the proportionality constant $K=(\eta/4q^2)$; actual annihilation time is the measured time between the start of the simulation and the annihilation of the chosen pair; log-log scale is used. Solid line has slope 1 (diffusive behavior), dashed line has slope 1.14 (measured—superdiffusive behavior).

fluctuations and, in some cases, acceleration of particle drift from areas with nonzero local net charge. The latter mechanism is working only when the long-range interaction is very strong (close to $n=1$) and system dimensionality is rather low (close to $d=2$). Thus, in the case $d=2$, $n=1$, at large times, particles are found to be traveling much larger distances than expected, and, in particular, mean-square displacement $\langle R^2 \rangle$ is proportional not to t, but to $t^{8/7}$, in agreement with our theory (for more details, see [8]). This phenomenon, to our knowledge, has not been observed before, and it is characteristic for all systems that belong to region A in Fig. 1. It should be seen, for example, in studies of XY systems quenched to very low temperatures (much lower than the Kosterlitz-Thouless [14] transition).

Region B corresponds to system with diffusion-type particle dynamics and slow annihilation. The decay exponent ν for all systems in this area is much less than 1 and is less than for systems with the same d of class A. This class includes case $n=\infty$, which is well known and theoretically explained.

Region C corresponds to systems with diffusion-type particle dynamics and mean-field decay behavior. For those systems, initial clusters of particles of one charge diffuse out quicker than $(1/t)$, so the system becomes well stirred even before significant annihilation could occur. Such systems are in a kinetic, rather than a diffusive, limit.

The borderline cases between regions B and C, which include the important case of ions in three dimensions, most likely are well described by the mean-field decay law. Nevertheless, there is a possibility of a logarithmic correction to the mean-field result.

The proposed scaling approach obviously fails for $d<2$ and strong interactions $(n<1)$. Indeed, the Gaussian system for $d=1$, for example, has $n=0$, and thus, a $(1/n)$ expansion is no longer applicable in the vicinity of this point.

In order to obtain better understanding of the role of long-range interactions in annihilation processes, it will be necessary to use the more elaborate $(1/n)$ expansion instead of the linear interpolation employed in this work. Such a task should require use of the renormalization group formalism, similar to that implemented in one-species annihilation problem [15,16].

This work was supported by NSF Solid State Chemistry Grant No. DMR 92-23729 and NASA Grant No. NAG3-1600.

[1] Ya. B. Zeldovich and A. A. Ovchinnikov, Chem. Phys. **28**, 215 (1978).
[2] K. Kang and S. Redner, Phys. Rev. Lett. **52**, 955 (1984).
[3] D. Toussaint and F. Wilczek, J. Chem. Phys. **78**, 2642 (1983).
[4] B. Yurke, A. N. Pargelis, T. Kovacs, and D. A. Huse, Phys. Rev. E **47**,m 1525 (1993).
[5] S. G. Entelis, *Reaction Kinetics in the Liquid Phase* (Wiley, New York, 1976).
[6] I. M. Sokolov and A. Blumen, Phys. Rev. E **50**, 2335 (1994); Europhys. Lett. **21**, 855 (1993).
[7] T. A. DeGrand and R. Loft, Phys. Rev. B **35**, 8528 (1987).
[8] W. G. Jang, V. Ginzburg, C. D. Muzny, and N. A. Clark, Phys. Rev. E **51**, 411 (1995).
[9] M. Mondello and N. Goldenfeld, Phys. Rev. A **42**, 5865 (1990).
[10] Of course, this division of particles into mobile and immobile is relative with respect to the selected domain size L and selection of the domain itself. Thus, when speaking about kinetics of mobile and immobile particles, we will always assume that selection of $L \gg d_0$ has been made and will relate everything to this length scale.
[11] G. H. Wannier, *Statistical Physics* (Dover, New York, 1987).
[12] F. Leyvraz, J. Phys. A **25**, 3205 (1992).
[13] M. Bramson and J. L. Lebowitz, Phys. Rev. Lett. **61**, 2097 (1988).
[14] J. M. Kosterlitz and D. J. Thouless, J. Phys. C **6**, 1181 (1973).
[15] L. Peliti, J. Phys. (Paris) **46**, 1469 (1985).
[16] L. Peliti, J. Phys. A **19**, L365 (1986).