Diffusion-Controlled Annihilation in the Presence of Particle Sources: Exact Results in One Dimension

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(Received 25 March 1985)

The steady-state particle density $\bar{n}$ and the relaxation time τ of homogeneous density fluctuations are calculated for one-dimensional systems in which particles move diffusively and annihilate irreversibly, and steady sources of either single particles (model I) or pairs of neighboring particles (model II) are also present. For small particle-production rates h, we find $\bar{n}\sim h^{1/\delta}$ and $\tau\sim h^{-\Delta}$ with $\delta=3$, $\Delta=\frac{2}{3}$ for model I and $\delta=2$, $\Delta=1$ for model II. If we interpret particles as solitons, model II is used to account for some aspects of the experimental data on the photoinduced absorption of *trans*-$(CH)_x$.

PACS numbers: 05.40. + j, 05.50. + q, 05.70.Ln

The principles of equilibrium statistical mechanics are well established and progress in describing near-equilibrium relaxational processes has also been remarkable.[1,2] Little is known, however, about the properties of systems which are either in or relaxing towards a far-from-equilibrium steady state. Given the importance and the difficulty of these nonequilibrium problems, one often tries to develop and study simple model systems which are mathematically transparent but at the same time show some resemblance to actual processes occurring in nature. In this paper, two such model systems will be considered and the exact calculation of the relevant steady-state and relaxational properties will be outlined.

The basic process is the same in both models. Particles execute a random walk (with hopping rate Γ per unit time) along a one-dimensional lattice and annihilate if they land on the same site simultaneously. This system would evolve into a trivial, completely empty state in the long-time limit ($t\to\infty$) and therefore to make the steady state more interesting we assume that particle sources are also present. The two models we consider are distinct in the mode of production of the particles. Single particles are created at a rate of Γh per lattice site in model I. In model II, on the other hand, the particles are produced in pairs at nearest-neighbor lattice sites and the rate of production is Γh per adjacent pair of lattice sites.

Model I may be regarded as a first approximation to the kinetics of the reaction $A+A\to 0$ in a one-dimensional chemical reactor with steady inflow and outflow of particles. It may also be viewed as a reference model for a class of aggregation processes which display common scaling properties. For example, one-dimensional models of aerosol formation[3] describing circumstances when the aggregation centers are generated by photo-oxidation and sedimentation processes make the larger clusters disappear from the system are expected[4] to be in one universality class with model I.

Model II is more closely related to a real system. In *trans*-polyacetylene, soliton-antisoliton pairs can be generated by photoexcitation.[5] The solitons and the antisolitons are quite free to move along one-dimensional chains and at elevated temperatures they execute a random walk under the influence of thermal fluctuations. Furthermore, since solitons alternate with antisolitons in this system, every meeting of two excitations results in annihilation. Thus identifying the solitons and antisolitons with the particles in model II one can see that, apart from the interactions between the soliton-antisoliton pairs, this model accounts for the essential features of the excitation dynamics of *trans*-$(CH)_x$.

It is intuitively clear (and can be proved for finite chains by making use of the Markovian nature of the processes[6]) that in the limit $t\to\infty$, both models I and II approach a steady state in which particle production is balanced by diffusive annihilation. This steady state and the relaxation towards it will be characterized on a macroscopic level by calculation of the steady-state particle density, $\bar{n}$, and the relaxation time, τ, governing the long-time decay of homogeneous density fluctuations. Both $\bar{n}$ and τ are functions of the relative feed rate, h, which is the only control parameter in the system (the hopping rate Γ just sets the time scale). Our results for $\bar{n}(h)$ and $\tau(h)$ are particularly simple in the small—feed-rate ($h\to 0$) limit where we find

$$\bar{n}(h)\sim h^{1/\delta},\quad \tau(h)\sim h^{-\Delta} \tag{1}$$

with

$$\delta=3,\quad \Delta=\tfrac{2}{3}\ \text{(model I)}, \tag{2}$$

$$\delta=2,\quad \Delta=1\ \text{(model II)}. \tag{3}$$

These results are in agreement with the available Monte Carlo data.[7] They also support the recently developed scaling theory of aggregation[4] in which the $h\to 0$ limit is considered as a critical point, h is regarded as an external field conjugate to the order parameter, and the order parameter is identified with the cluster density (particle density in our case). The scaling form suggested by this theory [$n(h,t)\sim h^{1/\delta}\psi(ht^{1/\Delta})$ with $\psi(x)\to\psi(\infty)=0$ for $x\to\infty$ and $\psi(x)\to x^{-1/\delta}$ for $x\to 0$] is motivated by a

scaling generalization of the Smoluchowski equation[4] and it yields not only Eq. (1) but it also predicts that, at $h=0$, the density of particles n decays with time as

$$n(h=0,t)\sim t^{-\zeta}, \tag{4}$$

where ζ is related to δ and Δ through $\Delta\zeta=1/\delta$. At $h=0$, models I and II coincide. The corresponding problem of diffusive annihilation has been investigated extensively[8,9] and the power-law decay [Eq. (4)] with $\zeta=\frac{1}{2}$ is known to be an exact result.[8] Hence one can conclude [see (2) and (3)] that the scaling law $\Delta\zeta=1/\delta$ holds for both models and, thus, one finds support for the view that the scaling description around the point $h=0$ is valid quite generally. The scaling theory[4] also yields a scaling relation, $\Delta+1/\delta=1$, which is less general. It is predicted to be valid only for model I where the kinetic coefficient in the generalized Smoluchowski equation describing the process is argued to be nonsingular in the $h\to 0$ limit.[4] As can be seen from (2), this prediction is also verified.

As in the case of critical phenomena, the components δ, Δ, and ζ are expected to be universal with respect to the details of the interactions; e.g., adding short-range interactions to the contact interaction present in models I and II should not change the value of the exponents. Thus we may assume that the results for model II can be compared with experimental data on *trans*-polyacetylene. In this system, the magnitude of the photoinduced absorption at appropriate wave numbers is presumed to be related to the density, $\bar{n}$, of the photogenerated solitons. Experiments[10] show that, for small incident photon flux I, the steady-state density $\bar{n}$ increases as $\bar{n}\sim I$ in agreement with our $\delta=2$ result [Eq. (3)]. Furthermore, the instantaneously induced bleaching is observed[11,12] to decay in the picosecond range as $t^{-1/2}$. If this decay is due to the annihilation of the soliton-antisoliton pairs then, as discussed in Refs. 9 and 12, the diffusive annihilation model ($h=0$ limit of model II) implies the observed $t^{1/2}$ behavior. Encouraged by these agreements we now make a prediction on the basis of Eq. (3). Namely, the result $\Delta=1$ means that, after one switches on the photon flux, the density of solitons and, consequently, the photoinduced absorption attain their steady-state value with a relaxation time τ which diverges as I^{-1} in the small flux limit. To our knowledge this relaxation time has not been measured yet. Clearly, if scaling ($\tau\sim I^{-1}$) is not confirmed by experiment, then alternative routes to soliton decay would have to be explored.

Now we turn to the derivation of results (2) and (3). The basic idea is the following. The particles are identified with the domain walls in the kinetic Ising model and the spin-flip probabilities are chosen so that the domain-wall dynamics will correspond to the particle dynamics of models I and II.

More precisely, we consider a system whose state $\{\sigma\}\equiv\{\ldots,\sigma_i,\sigma_{i+1},\ldots\}$ is specified by the stochastic spin variables $\sigma_i(t)=\pm 1$ assigned to lattice sites labeled by an integer $-\infty<i<\infty$. The correspondence between the spin and the particle configurations is given through the bond variables $n_i=(1-\sigma_i\sigma_{i+1})/2$. Site i is assumed to be occupied by a particle if $n_i=1$ (i.e., if there is a domain wall between sites i and $i+1$) and is regarded to be empty otherwise ($n_i=0$). The dynamics of the spin and, consequently, of the particle system is described by the probability distribution $P(\{\sigma\},t)$ satisfying the following master equation:

$$\dot{P}(\{\sigma\},t)=\sum_{i=-\infty}^{\infty}\sum_{\alpha=1}^{2}[w_i^{(\alpha)}(\{\sigma\}_i^{\alpha})P(\{\sigma\}_i^{\alpha},t)-w_i^{(\alpha)}(\{\sigma\})P(\{\sigma\},t)]. \tag{5}$$

Here the state $\{\sigma\}_i^1$ differs from $\{\sigma\}$ by a flipping of the ith spin and the flipping rate is given by

$$w_i^{(1)}(\{\sigma\})=\tfrac{1}{2}\Gamma[1-\tfrac{1}{2}\gamma\sigma_i(\sigma_{i+1}+\sigma_{i-1})]. \tag{6}$$

If no other spin-flip processes are present ($w_i^{(2)}\equiv 0$) then (5) and (6) define the exactly solvable kinetic Ising model[13] which relaxes to the equilibrium Ising model at temperature T provided $\gamma=\tanh(2J/kT)$ where J is the strength of the nearest-neighbor coupling. The implications of this spin-flip dynamics for the motion of the particles are especially simple at $T=0$ ($\gamma=1$). The particles move to left and right with equal rates $\Gamma/2$ and two nearest-neighbor particles annihilate at a rate Γ. Thus the $T=0$ limit of the kinetic Ising model gives the $h=0$ limit of models I and II.

To introduce the single-particle sources we assume that $\{\sigma\}_l^2$ in (5) differs from $\{\sigma\}$ by the simultaneous flipping of all the spins σ_l, $l\le i$, and that the rate of flipping is

$$w_i^{(2)}(\{\sigma\})=\Gamma h. \tag{7}$$

The above process creates particles homogeneously at a rate Γh per site and this process also obeys the rule that particle creation at an already occupied site is equivalent to emptying that site. Thus (5), (7), and (6) with $\gamma=1$ define a kinetic Ising model which generates the particle dynamics of model I.

Since there is no mechanism in this model which could produce an inhomogeneous steady state, the calculation of $\bar{n}$ and τ involves only translationally invariant states. Thus we shall assume that the initial distribution $P(\{\sigma\},0)$ and, as a consequence, $P(\{\sigma\},t)$ at arbitrary t is translationally invariant. Then the average particle density $n(h,\Gamma t)$ can be written as

$$n(h,\Gamma t)=(1-\langle\sigma_i\sigma_{i+1}\rangle)/2, \tag{8}$$

where the angular brackets denote averaging with respect to $P(\{\sigma\},t)$. The spin correlation function $\langle\sigma_i\sigma_{i+1}\rangle$ can be calculated because the two-point correlation functions $r_k(h,\Gamma t)=\langle\sigma_i\sigma_{i+k}\rangle$ satisfy a closed set of linear dif-

ferential equations. These equations are easily derived following the steps of Glauber's paper.[13] The result for $k>0$ is

$$\Gamma^{-1}\dot{r}_k = r_{k-1}+r_{k+1}-2(1+hk)r_k \ , \tag{9}$$

while for $k=0$ we have $r_0=\langle\sigma_i^2\rangle=1$ and for $k<0$, $r_k=r_{-k}$.

The stationary solution $\bar{r}_k(h)$ which is finite in the limit $k\to\infty$ is found by setting $\dot{r}_k=0$ in (9) and comparing the resulting equation with the recurrence relation satisfied by the Bessel functions[14] $J_\nu(z)$ of the first kind of order ν:

$$0=J_{\nu-1}(z)+J_{\nu+1}(z)-(2\nu/z)J_\nu(z) \ . \tag{10}$$

This comparison yields $\bar{r}_k(h)=CJ_{k+h^{-1}}(h^{-1})$ and the arbitrary constant C is determined from the condition $\bar{r}_0(h)=1$ giving $C^{-1}=J_{h^{-1}}(h^{-1})$. Substituting these results into (8) we obtain the steady-state density

$$\bar{n}(h)=[1-J_{1+h^{-1}}(h^{-1})/J_{h^{-1}}(h^{-1})]/2 \ . \tag{11}$$

The small-h behavior of $\bar{n}$ can be found by noting that for $\nu\to\infty$, $J_\nu(\nu+z\nu^{1/3})=2^{1/3}\nu^{-1/3}\,\mathrm{Ai}(-2^{1/3}z)+O(\nu^{-1})$ where $\mathrm{Ai}(z)$ is the Airy function.[14] The result is

$$\bar{n}=-\frac{\mathrm{Ai}'(0)}{2^{2/3}\,\mathrm{Ai}(0)}, \quad h^{1/3}=0.4593h^{1/3} \ , \tag{12}$$

yielding $\delta=3$ as quoted in (2).

To obtain the relaxation times of homogeneous density fluctuations, we seek solutions to (9) in the form

$$r_k=\bar{r}_k+q_k e^{-2\lambda\Gamma t} \ . \tag{13}$$

Substituting (13) into (9) one finds that the set of equations for q_k is the same as that for r_k except that $1+kh$ is replaced by $1-\lambda+kh$. Hence a comparison with (10) yields $q_k=AJ_{k+(1-\lambda)h^{-1}}(h^{-1})$ and the "boundary" condition $q_0=0$ following from $r_0=\bar{r}_0=1$ gives the equation which determines the possible values of λ:

$$J_{(1-\lambda)h^{-1}}(h^{-1})=0 \ . \tag{14}$$

All the solutions $\lambda_i(h)$ of this equation are greater than zero since the zeros j_i^ν of $J_\nu(z)$ on the positive real axis satisfy[14] the inequality $\nu<j_i^\nu$. Consequently, all the homogeneous density perturbations decay with time exponentially. The analysis of the limit $h\to0$ is again carried out by using the limit $\nu\to\infty$ of $J_\nu(\nu+z\nu^{1/3})$. In this limit, Eq. (14) transforms into

$$\mathrm{Ai}[-2^{1/3}h^{-2/3}\lambda/(1-\lambda)^{1/3}]=0 \tag{15}$$

and using the fact that the zeros of the Airy function, $\mathrm{Ai}(a_j)=0$, are on the negative real axis ($a_j<a_1<0$) one can conclude that (a) in the limit $h\to0$ no solution λ_j of Eq. (15) approaches zero faster than $h^{2/3}$ and (b) there is an infinite set of λ which goes to zero as $\lambda_j=2^{-1/3}|a_j|^{2/3}$. The relaxation time which governs the long-time decay of homogeneous density fluctuations is then determined by the smallest among the λ_j:

$$\tau^{-1}=2^{2/3}|a_1|\Gamma h^{2/3}=3.7115\Gamma h^{2/3} \ , \tag{16}$$

and so we have the results $\Delta=\frac{2}{3}$ [Eq. (2)].

Turning to model II, consider the spin dynamics defined by setting $w_i^{(2)}\equiv0$ in (5) and choosing

$$\gamma=(1-h)/(1+h), \quad 0\le h<\infty \ , \tag{17}$$

in (6). The dynamics of the corresponding particle system (model III) consists of the following processes: hopping to left and right with the rate $\Gamma/2$, annihilation of neighboring particles at a rate $\Gamma/(1+h)$, and production of nearest-neighbor particles at a rate $\Gamma h/(1+h)$. For small h, this is just the dynamics of model II. At larger h the rate of the annihilation of the neighboring particles is reduced with respect to the rate of hopping. This delay in the hopping of neighboring particles towards each other might be interpreted as the appearance of an effective short-range repulsion between the particles. Such a short-range interaction is not expected to generate a difference between the scaling properties of models II and III especially since the interaction disappears in the limit $h\to0$.

The small-h behavior of $\bar{n}$ and τ in model II can now be obtained from model III which is the exactly solvable kinetic Ising model with $\gamma=\tanh(2J/kT)$ related to the rate h of the particle production through Eq. (17) yielding $h=\exp(-4J/kT)$. Since the kinetic Ising model relaxes to the equilibrium Ising model, $\bar{n}$ is determined by the equilibrium correlation $\langle\sigma_i\sigma_{i+1}\rangle_{\mathrm{eq}}=\tanh(J/kT)$ with the result

$$\bar{n}=h^{1/2}/(1+h^{1/2})\approx h^{1/2} \ , \tag{18}$$

implying $\delta=2$ as claimed in (3). The calculation of τ is also simple since $\langle\sigma_i\sigma_{i+1}\rangle$ is proportional to the energy of the Ising model and we need only to determine the long-time decay of homogeneous energy perturbations. This has been done[15] and for the slowest mode of decay one has

$$\tau^{-1}=2\Gamma(1-\gamma)=4\Gamma h/(1+h)\approx4\Gamma h \ , \tag{19}$$

yielding $\Delta=1$. This completes the derivation of results (2) and (3).

Finally, we note that the steady-state distribution function

$$P_s(\{n\})=P_s(\ldots,n_i,n_{i+1},\ldots)$$

for the particles in model III can also be calculated since it is just the distribution function of the corresponding Ising model,

$$P_I(\{\sigma\})=Z^{-1}\exp[(J/kT)\textstyle\sum_i\sigma_i\sigma_{i+1}]$$

expressed in terms of the bond variables n_i as follows:

$$P_s(\{n\})=P_I(\{n\})=\textstyle\prod_i\exp(a+bn_i) \tag{20}$$

with $a=-\ln(1+h^{1/2})$ and $b=\ln h^{1/2}$. Thus the steady state can be described in terms of independent two-state objects which are in equilibrium with a heat bath. This means that the detailed-balance condition is satisfied in this steady state. While detailed balance is a necessary feature of equilibrium processes, its appearance in a nonequilibrium stationary process is unusual. In this sense, model III defines a rather uncommon nonequilibrium dynamics and it would certainly be more valuable if one could calculate the steady-state distribution for model I where the possibility of detailed balance is excluded by construction.

This work was supported by the National Science and Engineering Research Council of Canada. I would like to thank M. Plischke for helpful conversations.

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