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LETTER TO THE EDITOR

Smoluchowski and beyond: a field theoretical study of coagulation/fragmentation processes

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Abstract. Adopting simple field theoretical techniques we demonstrate how the Smoluchowski approach to reaction-diffusion models can be systematically corrected. Focusing on coagulation/fragmentation processes we identify the upper critical dimension $d_c = 2$ below which finite mobility corrections are important and full universality (lattice independence, etc) can be achieved. Trends seen by direct simulation of simple lattice models for $d > 2$ are confirmed, whilst problems of interpretation exist for $d < 2$.

Coagulation and fragmentation processes are central to our understanding of many diverse physical, chemical or biological systems. Applications arise, for example, in polymer and colloidal science (Friedlander 1977), antigen-antibody aggregation (Johnston and Benedek 1984) and cluster formation in galaxies (Silk 1980). To model these systems the Smoluchowski (1917) approach, which may be characterised as the simplest mean-field (or infinite mobility) approximation, is often used, whilst more recently there has been a trend towards the direct simulation of simple lattice models. Scaling predictions based on the Smoluchowski rate equations generally find support both from experiment (Weitz and Lin 1986) and from numerical simulations, as one would expect for $d > d_c$, the upper critical dimension. In particular simulations by Family *et al* (1986) of the coagulation/fragmentation reaction

$$X_r + X_s \underset{k}{\overset{p}{\rightleftharpoons}} X_{r+s} \tag{1}$$

suggest that if $k \neq 0$, $d_c < 1$, whilst for $k = 0$, $d_c = 2$ (Vicsek and Family 1984). We disagree. Adopting field theoretical techniques recently developed (Elderfield 1985a, b, Grassberger and Scheunert 1980, Peliti 1985) we shall argue for $d_c = 2$ in both cases. Broadly the scaling behaviour is representative of a 'tricritical' Schlögl model (Elderfield and Vvedensky 1985 and references therein), whilst if $k = 0$ the model is closely related to the diffusive annihilation model discussed by Peliti (1986). To understand this discrepancy one must presume that the $d = 1$ simulations of Family *et al* (1986) relate only to the strong diffusion regime for which the Smoluchowski rate equations always apply if $d > 0$. Our field theory contains a pure diffusive mode associated with the conserved density $m(\boldsymbol{r}, t) = \Sigma_k k\rho_k$, where $\rho_k(\boldsymbol{r}, t)$ is the density of k-mers, as one would expect. It is interesting, however, to observe that a novel Lagrangian symmetry is associated with this property and thus one has a Goldstone mode. Happily we can show that the physics is only weakly modified by this Goldstone for $d > 2$, whilst for $d < 2$ it is important but controllable.

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Given the coagulation/fragmentation reaction (1) it is natural to introduce the following spatially discrete Markovian reaction-diffusion equation (Gardiner 1983):

$$\frac{\partial P}{\partial t}(\{X_k(i)\}, t) = \sum_{i,j=1}^{N} D_{ij} \sum_{r=1}^{\infty} ((X_r(i)+1)P(\{X_k(l)\}_{k\neq r}^{l\neq i,j}, X_r(i)+1, X_r(j)-1, t)$$

$$- X_r(i)P(\{X_k(l)\}, t))$$

$$+ \tfrac{1}{2} \sum_{i=1}^{N} \sum_{r,s}^{\infty} p_{rs}((X_r(i)+1)(X_s(i)+1)P(\{X_k(l)\}_{k\neq r,s,r+s}^{l\neq i}, X_{r+s}(i)-1,$$

$$X_r(i)+1, X_s(i)+1, t) - X_r(i)X_s(i)P(\{X_k(l)\}, t))$$

$$+ \tfrac{1}{2} \sum_{l=1}^{N} \sum_{r,s}^{\infty} k_{rs}((X_{r+s}(i)+1)P(\{X_k(l)\}_{k\neq r,s,r+s}^{l\neq i}, X_{r+s}(i)+1, X_r(i)-1, t)$$

$$- X_{r+s}(i)P(\{X_k(l)\}, t)) \tag{2}$$

where $X_r(i)$ is the number of molecules of mass r in the ith spatial cell. The non-local terms represent cell to cell diffusion whilst the local terms are specified by the reaction (1). To solve equations such as (2) we seek solutions in the form of a Poisson transform (Gardiner and Chaturvedi 1977, Elderfield 1985a)

$$P(\{X_r(i)\}, t) = \int_{\mathscr{C}} \prod_{i=1}^{N} \prod_{r=1}^{\infty} \left(d\alpha_r(i) \exp(-\alpha_r(i)) \frac{\alpha_r(i)^{X_r(i)}}{X_r(i)!} \right) f(\{\alpha_r(i)\}, t) \tag{3}$$

where $\mathscr{C}$ is a closed contour in the complex plane and as such $f(\{\alpha_r(i)\})$ is best viewed as a Markovian quasi-probability. Direct substitution of (3) into (2) leads to the *exact* Fokker-Planck description

$$\frac{\partial f}{\partial t}(\{\alpha_r(i)\}, t) = - \sum_{i,j=1}^{N} \sum_{r=1}^{\infty} \frac{\partial}{\partial \alpha_r(i)} (D_{ij}\alpha_r(j) f(\{\alpha_r(i)\}, t))$$

$$- \sum_{i=1}^{N} \tfrac{1}{2} \sum_{r,s=1}^{\infty} \left[\left(1 - \frac{\partial}{\partial \alpha_r(i)}\right)\left(1 - \frac{\partial}{\partial \alpha_s(i)}\right) - \left(1 - \frac{\partial}{\partial \alpha_{r+s}(i)}\right) \right]$$

$$\times (p_{rs}\alpha_r(i)\alpha_s(i) - k_{rs}\alpha_{r+s}(i)) \tag{4}$$

which for our purposes is best redeveloped into a part integral form. Adopting a variant of the Martin-Siggia-Rose formalism one obtains a generating functional $Z(\hat{l}, l)$ for the Poisson correlation and response functions in the form (Elderfield 1985a, b, Elderfield and Vvedensky 1986)

$$Z(\hat{l}, l) = \int [d\hat{\alpha}] \int [d\alpha] \exp\left(\int dt (L + l\alpha + \hat{l}\hat{\alpha}) \right) \tag{5}$$

where the Lagrangian L is given in the continuum limit ($a \to 0$) by

$$L = \int d\boldsymbol{r}^d \left(\sum_r i\hat{\alpha}_r(\boldsymbol{r}, t) \left(-D\nabla^2 + \frac{\partial}{\partial t} \right) \alpha_r(\boldsymbol{r}, t) \right.$$

$$- \tfrac{1}{2} \sum_{r,s} [(1 - i\hat{\alpha}_r(\boldsymbol{r}, t))(1 - i\hat{\alpha}_s(\boldsymbol{r}, t)) - (1 - i\hat{\alpha}_{r+s}(\boldsymbol{r}, t))]$$

$$\left. \times (a^d p_{rs}\alpha_r(\boldsymbol{r}, t)\alpha_s(\boldsymbol{r}, t) - k_{rs}\alpha_{r+s}(\boldsymbol{r}, t)) \right). \tag{6}$$

Here $\alpha_s(\boldsymbol{r}) = \alpha_s(i)/a^d$, $\hat{\alpha}(\boldsymbol{r}) = \hat{\alpha}_s(i)$ and 'a' is the primitive cell size.

As one might anticipate, Poisson correlation and response functions are given by

$$\langle \alpha_s(\boldsymbol{r}, t)\rangle = \frac{\partial}{\partial l_s(\boldsymbol{r}, t)} Z(\hat{l}, l)\Big|_{\hat{l}=l=0}$$

$$\langle \alpha_s(\boldsymbol{r}, t)\alpha_p(\boldsymbol{r}', t')\rangle = \frac{\partial^2}{\partial l_s(\boldsymbol{r}, t)\partial l_p(\boldsymbol{r}', t')} Z(\hat{l}, l)\Big|_{\hat{l}=l=0} \qquad (7)$$

$$\vdots \qquad\qquad \vdots$$

Of course only the concentration fluctuations are of direct physical interest. Happily for equal-time correlations, simple connection formulae are evident from (3)

$$\langle\!\langle \rho_s(\boldsymbol{r}, t)\rangle\!\rangle = \langle \alpha_s(\boldsymbol{r}, t)\rangle$$

$$\langle\!\langle \rho_s(\boldsymbol{r}, t)\rho_p(\boldsymbol{r}', t)\rangle\!\rangle = \langle \alpha_s(\boldsymbol{r}, t)\alpha_p(\boldsymbol{r}', t)\rangle + \delta(\boldsymbol{r}-\boldsymbol{r}')\delta_{ps}\langle \alpha_s(\boldsymbol{r}, t)\rangle \qquad (8)$$

$$\vdots \qquad\qquad \vdots \qquad\qquad \vdots$$

whilst for multi-time functions generalisations have been derived by Elderfield (1985a).

Given the Lagrangian L, it is now a fairly simple task to both recover the Smoluchowski rate equations and discuss the corrections associated with finite mobility ($D^{-1} \neq 0$). The deterministic or mean-field approximation is defined by

$$\partial L/\partial \hat{\alpha} = 0 \qquad (9)$$

with $\hat{\alpha} = 0$, trivially (see de Dominicis and Peliti 1978, Elderfield 1985c). Performing the differentiation one finds directly the Smoluchowski equations in the form

$$\frac{\partial \rho_s}{\partial t} - D\nabla^2 \rho_s = \tfrac{1}{2} \sum_{\substack{l,m \\ l+m=s}}^{\infty} (a^d p_{lm}\rho_l\rho_m - k_{lm}\rho_{l+m}) - \sum_{m=1}^{\infty} (a^d p_{ms}\rho_m\rho_s - k_{ms}\rho_{m+s}) \qquad (10)$$

where we have used the connection formulae (8) to introduce ρ_r, the density of molecules with mass r. For $D \to \infty$ the spatial term may be dropped, for homogeneity is then ensured at all length scales. In this way we reproduce the Smoluchowski equation quoted by Family *et al* (1986).

To discuss the finite mobility corrections to (10) it is helpful to first suppress the 'internal' degrees of freedom and study the model Lagrangian L^*:

$$L^* = \int \mathrm{d}\boldsymbol{r}^d \left(\mathrm{i}\hat{\alpha}\left(\frac{\partial}{\partial t} - D\nabla^2\right)\alpha - [(1-\mathrm{i}\hat{\alpha})^2 - (1-\mathrm{i}\hat{\alpha})](k\alpha - pa^d\alpha^2)\right). \qquad (11)$$

Rescaling $\hat{\alpha}$, α this may for $k \neq 0$ be thrown into a symmetrised form reminiscent of a Schlögl model (Elderfield and Vvedensky 1985)

$$L_s = \int \mathrm{d}\boldsymbol{r}^d \left[\mathrm{i}\hat{\alpha}\left(\frac{\partial}{\partial t} - D\nabla^2 + k\right)\alpha - a^{d/2} g(\mathrm{i}\hat{\alpha}\alpha^2 + \hat{\alpha}^2\alpha) - pa^d(\hat{\alpha}\alpha)^2 \right] \qquad (12)$$

where the cubic coupling g satisfies $-g^2 = pk$. For $k \to 0$ at finite g, p this model exhibits the simplest non-equilibrium continuous phase transition. One finds that $d_c = 4$ and the universality class is that of directed percolation or Reggeon theory. However in the present case g depends strongly on k so that the physics of fragmentation/coagulation is very different. Let us consider for example the equation of motion (Brézin *et*

al 1976). For the Lagrangian L_s one finds

$$\left(\frac{\partial}{\partial t} - D\nabla^2 + k\right)M(\boldsymbol{r}, t) - \left[a^{d/2}g\left(\frac{\partial\Gamma}{\partial v(\boldsymbol{r}, t)} - \frac{\partial\Gamma}{\partial k(\boldsymbol{r}, t)}\right) + pa^d\frac{\partial\Gamma}{\partial w(\boldsymbol{r}, t)}\right]_{\substack{v,w=0\\k(\boldsymbol{r},t)=k}} = \frac{\partial\Gamma}{\partial\hat{M}(\boldsymbol{r}, t)}. \tag{13}$$

Here $\Gamma(\hat{M}, M)$ is the vertex generator given by

$$\Gamma(\hat{M}, M) = \ln Z(\hat{l}, l) = \hat{M}\hat{l} - Ml \equiv \sum_{r,s}\frac{(\hat{M})^r}{r!}\frac{(M)^s}{s!}\Gamma^{rs} \tag{14}$$

and v, w are associated with source terms $v\alpha^2$, $iw\hat{\alpha}\alpha^2$ we introduce into L_s. Now $M = \langle\alpha\rangle$ is precisely the density ρ (see (8)), whilst $\hat{M} = 0$, so a low density approximation yields the dynamical equation

$$\left(\frac{\partial}{\partial t} - D\nabla^2 + k\right)\rho(\boldsymbol{r}, t) = g\int d\boldsymbol{r}'^d\int dt'\int d\boldsymbol{r}''^d\int dt''\, A(\boldsymbol{r}, t\,|\,\boldsymbol{r}', t', \boldsymbol{r}'', t'')\rho(\boldsymbol{r}', t')\rho(\boldsymbol{r}'', t'') + O(\rho^3) \tag{15}$$

where the effective interaction is given by

$$A(\boldsymbol{r}, t|\boldsymbol{r}', t', \boldsymbol{r}'', t'') \equiv \frac{\partial\Gamma^{0,2}}{\partial v(\boldsymbol{r}, t)}(\boldsymbol{r}', t', \boldsymbol{r}'', t'') = \left[1 + \text{  } + \text{  } + 2\text{ loops}\right]\ldots. \tag{16}$$

Notice that the other terms evident from (13) vanish identically because they do not break the important symmetry

$$\hat{\alpha}(t) \rightleftharpoons \alpha(-t) \tag{17}$$

evident from (12). In this way we obtain perturbative control of the finite mobility corrections to the Smoluchowski rate equations, which correspond here to the tree level, mean-field or deterministic approximation. We are primarily interested in stationary homogeneous solutions of (15) so it is sufficient to focus on the long-wavelength low-frequency behaviour of the effective reactivity A (16). Analysing the perturbative development (16) it is clear that the structure of A depends strongly on two dimensionless couplings z_S, z_A associated, respectively, with the cubic (Schlögl) and quartic (annihilation, $X + X \to 0$) couplings. We shall naturally assume that the diffusion constant D satisfies

$$1/L^2 \ll k/D \ll 1/a^2 \tag{18}$$

where L, 'a' are length scales characteristic of the reaction vessel and the underlying lattice, respectively. The left-hand inequality implies that the model is not trivially 'zero dimensional' and sensitive to boundary conditions, whilst the right bound is necessary but *not sufficient* to eliminate the lattice effects. As one would expect the behaviour of the reactivity A depends strongly on the spatial dimension. We find the following structures as d decreases.

(i) $d > 4$. The theory is non-renormalisable and A depends strongly on the underlying lattice. Happily, however, for this case (16) corresponds to a perturbative development in terms of dimensionless couplings

$$z_S = g^2a^4/D^2 \qquad z_A = pa^2/D \tag{19}$$

so at high mobilities $D \to \infty$, the corrections are small.

(ii) $4 > d > 2$ The cubic coupling g is renormalisable leading only to a weak lattice dependence. One has

$$z_S = \left(\frac{ga^2}{D}\right)^2 \left(\frac{ka^2}{D}\right)^{(d-4)/2} \tag{20}$$

which leads to Schlögl-like scaling for $k \to 0$, g finite. For our case, however, $-g^2 = kp$, so we have

$$z_S = \left(\frac{pa^2}{D}\right)\left(\frac{ka^2}{D}\right)^{(d-2)/2} \tag{21}$$

and thus given (18), only weak corrections at high mobility. The quartic coupling p is, by contrast, non-renormalisable, so the $d > 4$ behaviour persists, leading to weak corrections in terms of z_A:

$$z_A = pa^2/D. \tag{22}$$

(iii) $d < 2$. The theory is finally fully renormalisable so that A is only very weakly dependent on the lattice, with z_S, z_A given by

$$z_S = z_A = \left(\frac{pa^2}{D}\right)\left(\frac{ka^2}{D}\right)^{(d-2)/2}. \tag{23}$$

In order to assign the upper critical dimension to such a theory we consider two features evident from the above. First we would only expect to see fully universal scaling for $d < 2$, since only then is the theory fully renormalisable and hence insensitive to lattice effects. Secondly, and for our purposes more importantly, we observe that the domain of validity of the Smoluchowski rate equations is more strongly controlled by (23) for $d < 2$ than by (19) or (20) for $d > 2$, given that to maintain lattice independence one must assume $ka^2/D \ll 1$ (18). For this model it would thus seem to be clear that $d_c = 2$, in spite of the claim of Family *et al* (1986) that $d_c < 1$ for $k \neq 0$. To understand this discrepancy one must presume that the $d = 1$ simulations of these authors relate only to the strong diffusion regime $D \to \infty$ for which the Smoluchowski approach is always appropriate if $d > 0$ (see (19), (21)-(23)).

Reintroducing the internal degrees of freedom, the above argument is, with one proviso, simply generalised, for the mass matrix associated with the field theory is proportional to k. Associated with the conserved density $m = \Sigma_k k\rho_k(r)$ there is a 'Goldstone' or pure diffusion mode, which implies that the Green function G ($\sim\!\!\sim$) appearing in equation (16) takes the form

$$G = \sim\!\!\sim = \frac{|\psi_0\rangle\langle\psi_0|}{Dq^2 + i\omega} + \sum_p \frac{|\psi_p\rangle\langle\psi_p|}{Dq^2 + \lambda_p + i\omega} \tag{24}$$

where the masses $\lambda_p \sim k$ are the non-zero eigenvalues of the mass matrix M_{ab}.

$$M_{ab} \equiv \left.\frac{\partial^2 L}{\partial(i\hat{\alpha}_a)\,\partial\alpha_b}\right|_{\hat{\alpha}=\alpha=0} - \delta_{ab}\left(\frac{\partial}{\partial t} - D\nabla^2\right) = \delta_{ab} \sum_{\substack{r,s \\ r+s=a}} k_{rs} - k_{a,b-a} \equiv \left[\begin{array}{c} \\ 0 \end{array}\right]_{ab} . \tag{25}$$

As one might expect $\langle\psi_k|$, $|\psi_k\rangle$ are simply the left- and right-hand eigenfunctions of M and in particular $\langle\psi_0| = (1, 2, 3, \ldots)$, $|\psi_0\rangle = (1, 0, 0 \ldots)$. For canonical choice $k_{rs} = (r+s)^\beta$ for some β corresponding to tree-like clusters (Family *et al* 1986), and all the eigenvalues λ_p are positive as desired. Introducing (24) into the graphical expansion

(16) for the effective interaction A it might seem that this Goldstone is dangerous for $d<4$. Happily, however, this conclusion is premature. Making the decomposition

$$\boldsymbol{\alpha}-\alpha_0|\psi_0\rangle=\beta \qquad \hat{\boldsymbol{\alpha}}-\hat{\alpha}_0\langle\psi_0|=\tilde{\boldsymbol{\beta}} \tag{26}$$

and simply ignoring the 'massive' components $\beta, \hat{\beta}$ as a first approximation, one is led to the following effective Lagrangian for the Goldstone mode $\hat{\alpha}_0, \alpha_0$

$$L_G=\int \mathrm{d}r^d\left[\mathrm{i}\hat{\alpha}_0\left(\frac{\partial}{\partial t}-D\nabla^2\right)\alpha_0+a^d p(\hat{\alpha}_0\alpha_0)^2\right]. \tag{27}$$

This Lagrangian L_G is closely related to a class described recently by Elderfield and Wilby (1987) and has a number of interesting properties. One finds that $d_c=2$ and moreover there exists an infrared stable fixed point in $d=2-\varepsilon$ for the associated renormalisation group equations. Consequently, the Goldstone is important but *not dangerous* for $d<2$ and can be ignored for $d>2$. It is of course important that the Lagrangian L_G cannot generate a mass dynamically, so we must now consider the influence of the massive fluctuations $\hat{\beta}, \beta$ (26). Fortunately, associated with the conserved density $m=\Sigma_m k\rho_t(\boldsymbol{r}, t)$ there is a novel Lagrangian symmetry:

$$\begin{aligned}
&\hat{\alpha}_k\to \mathrm{e}^{k\lambda}(\hat{\alpha}_k-1)+1\\
&\alpha_k\to \mathrm{e}^{-k\lambda}\alpha_k\\
&l_k\to l_k\,\mathrm{e}^{-k\lambda}+\mathrm{i}\,\mathrm{e}^{-k\lambda}\left(\frac{\partial}{\partial t}-D\nabla^2\right)\\
&l_k\to l_k\,\mathrm{e}^{k\lambda}
\end{aligned} \tag{28}$$

from which one can formulate Ward identities of the form

$$\frac{\partial Z}{\partial\lambda}(\hat{l}(\lambda), l(\lambda))=0. \tag{29}$$

Evaluating (29) using (28) and (6) one finds the desired diffusion equation

$$\left(\frac{\partial}{\partial t}-D\nabla^2\right)m(\boldsymbol{r}, t)=0. \tag{30}$$

To summarise we have argued that generally for coagulation/fragmentation reactions $d_c=2$, with deviations from the Smoluchowski rate predictions most evident for $k\to 0$. The scaling behaviour for $d<2$ can be broadly classified as tricritical in that weak Schlögl singularities ($d_c=4$, $X+X\rightleftharpoons X$) mix with those associated with diffusive annihilation ($d_c=2$, $X+X\to 0$). Additionally the system contains a Goldstone or pure diffusive mode, which is important but not uncontrollable for $d<2$ and ignorable above. Our conclusions are in accord with simulations for $d>2$ by Family *et al* (1986) or Viscek and Family (1984), but point to discrepancies in $d=1$. We presume that the one-dimensional simulations relate only to the strong diffusion regime $D\to\infty$ to which the Smoluchowki description is always appropriate if $d>0$.

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