Rate-equation approach to irreversible island growth with cluster diffusion

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A self-consistent rate-equation (RE) approach to irreversible island growth and nucleation is presented which takes into account cluster mobility. As a first application, we consider the irreversible growth of compact islands on a two-dimensional surface in the presence of monomer deposition (with rate F) and monomer diffusion (with rate D_1) while the mobility of an island of size s is assumed to satisfy $D_s = D_1 s^{-\mu}$ where $\mu > 0$. Results are obtained for the dependence of the island-density and island-size distribution (ISD) on the parameters D_1/F, μ, and coverage θ. For all values of μ, we find excellent agreement between our self-consistent RE results and simulation results for the island and monomer densities, up to and even somewhat beyond the coverage corresponding to the peak island density. We also find good agreement between our self-consistent RE and simulation results for the portion of the ISD corresponding to island sizes less than the average island-size S. However, for larger island sizes the effects of correlations become important and as a result the agreement is not as good. Using our self-consistent RE approach we also demonstrate that the discrepancies between simulations and recent mean-field predictions for the exponent $\tau(\mu)$ describing the power-law size dependence of the ISD for $\mu < 1$ can be explained almost entirely by geometric effects. Our results are also compared with those obtained using a simpler mean-field Smoluchowski approach. In general, we find that, except for the case $\mu = 1/2$ (for which the island and monomer densities are reasonably well predicted), such an approach leads to results which are in poor agreement with the simulations.

I. INTRODUCTION

Aggregation processes play an important role in many areas of science and technology and have applications including colloid science, aerosol physics, astrophysics, cloud dynamics, and chemical engineering. One of the most important theoretical approaches used is the mean-field rate-equation approach originally developed by Smoluchowski [1]. A variety of studies of the scaling behavior in aggregation processes have been carried out based on this assumption. However, there has been less emphasis on the quantitative evolution of the cluster density and cluster-size distribution.

A related problem is the evolution of the island-density and island-size distribution as a function of coverage in submonolayer epitaxial growth. In this case it is generally assumed that only monomers or very small islands are mobile, while clusters above a certain size do not diffuse. Based on this assumption, a self-consistent rate-equation (RE) approach [2] has been developed by which the island and monomer densities can be accurately calculated in the precoalescence regime. While this method was originally developed for the case of irreversible growth, it has since been extended [3,4] to reversible growth, and has also been further extended to make accurate predictions of the island-size distribution and size dependence of the island capture numbers [5–7]. While there have been some attempts [8] to extend the Bales and Chrzan [2] self-consistent RE approach to mobile clusters, no fully quantitative and/or self-consistent method has so far been developed.

Here we present a generalization of the self-consistent RE method of Bales and Chrzan to the case of irreversible submonolayer growth in the presence of cluster diffusion. As a specific application, we consider a model of submonolayer growth in which all islands are assumed to diffuse with diffusion coefficient $D_s = D_1 s^{-\mu}$ (where s is the number of

particles in a cluster). We note that one of the motivations for this work is the existence of recent experiments [9] on the growth of (compact) colloidal nanoparticle islands at a liquid-air interface in which significant cluster diffusion has been observed. However, cluster diffusion has also been found to be important in epitaxial graphene growth [10–12]. In addition, in previous studies a variety of different possible mechanisms for the diffusion of epitaxial clusters have been considered [13–19], which imply the existence of a power-law dependence of the diffusion coefficient on cluster size. These include cluster diffusion via uncorrelated evaporation-condensation ($\mu = 1/2$), correlated evaporation-condensation ($\mu = 1$), and periphery diffusion ($\mu = 3/2$). We note that the case $\mu = 1/2$ also corresponds to the Brownian (Stokes-Einstein) diffusion of compact two-dimensional (2D) clusters in two dimensions.

Accordingly, as a first application of our method, here we present a comparison between our self-consistent RE results and kinetic Monte Carlo (KMC) simulations for a variety of values of μ including $\mu = 1/2$ (Brownian diffusion) as well as for higher values of μ. For comparison, results for the case $\mu = \infty$ corresponding to no cluster-diffusion are also presented. In general we find that, using our self-consistent RE method, the island and monomer densities are accurately predicted up to and even significantly beyond the coverage corresponding to the peak island density for all values of μ considered. In addition, we find that for small values of μ ($\mu \leqslant 2$) there is excellent agreement between our RE results for the island-size distribution (ISD) and simulation results, although the effects of correlations (which are not included in our RE approach) appear to become more important with increasing μ. In particular, we find that while our RE results give good predictions for the small-s tail corresponding to "raw" islands for $\mu > 2$, the agreement is not as good for the peak of the distribution corresponding to large "ripe" islands.

We note that this is consistent with the results of Bales and Chrzan [2] for the case of immobile islands ($\mu = \infty$) for which it was found that correlations between the size of an island and the size of the surrounding capture zone (which are not included in the RE approach) lead to significant discrepancies between the ISD predicted from RE's and KMC simulations.

Our RE results also demonstrate that the discrepancies between recent theoretical predictions for the exponent $\tau(\mu)$ describing the size dependence of the ISD for $\mu < 1$ can be explained almost entirely by geometric effects. For comparison, we also present RE results corresponding to the "constant capture number" Smoluchowski assumption $K_{ij} = \sigma_0(D_i + D_j)$ [1,20,21]. In general, we find that, except for the case $\mu = 1/2$ (for which the island and monomer densities are reasonably well predicted), such an approach leads to results which are in poor agreement with simulations.

The organization of this paper is as follows. In Sec. II we present our self-consistent RE approach while in Sec. III we briefly discuss the model [22] used in our KMC simulations. In Sec. IV we then present our RE results and compare with simulations. Finally, in Sec. V we discuss our results.

II. SELF-CONSISTENT RATE-EQUATION APPROACH

Assuming that N_s is the density of islands of size s and θ is the coverage, then for the case of cluster-diffusion and irreversible aggregation in the presence of monomer deposition, we may consider the following set of rate equations,

$$\frac{dN_s}{d\theta} = \delta_{s,1}\left(1 - \sum_{i=1}^{\infty}\kappa_i N_i\right) + \frac{1}{2}\sum_{i+j=s} K_{i,j}N_i N_j/F$$
$$-N_s\sum_{i=1}^{\infty}K_{s,i}N_i/F, \qquad (1)$$

where $K_{i,j}(\theta)$ is the aggregation kernel for a cluster of size i and size j to aggregate to form a cluster of size $i + j$ and the terms with κ_i [where $\kappa_i = (1 + \delta_{1,i})\frac{\pi}{4}(\sqrt{s} + 1)^2$ for the circular islands considered here] correspond to the direct impingement of monomers on an island of size i. Without loss of generality we may rewrite the aggregation kernel in the form

$$K_{ij}(\theta) = D_i\sigma_{ij}(\theta) + D_j\sigma_{ji}(\theta), \qquad (2)$$

where D_i corresponds to the diffusion rate for a particle of size i and σ_{ij} is the "capture number" for a cluster of size i by a cluster of size j. Defining the ratio $R_i = D_i/F$, Eq. (1) may be rewritten more compactly as

$$\frac{dN_s}{d\theta} = \mathcal{J}_s - R_s N_s/\xi_s^2, \qquad (3)$$

where

$$\mathcal{J}_s = \delta_{s,1}\left(1 - \sum_{i=1}^{\infty}\kappa_i N_i\right) + \frac{1}{2}\sum_{i+j=s}(R_i\sigma_{ij} + R_j\sigma_{ji})N_i N_j$$
$$-N_s\sum_{i\neq s}^{\infty}R_i\sigma_{is}N_i - \Delta\left[R_s\sigma_{ss}N_s^2\right], \qquad (4)$$

and

$$\frac{1}{\xi_s^2} = (1 - \Delta)\sigma_{ss}N_s + \sum_{i=1}^{\infty}\sigma_{si}N_i. \qquad (5)$$

We note that the terms with Δ in Eqs. (4) and (5) above indicate different possible ways to apportion the RE term $2R_s\sigma_{ss}N_s^2$ [corresponding to the "capture" of a cluster of size s by another cluster of size s] among the two terms $\mathcal{J}_s$ and R_sN_s/ξ_s^2 of Eq. (3). In particular, assuming $\Delta = 0$ is consistent with the previous work of Bales and Chrzan [2], while assuming $\Delta = 1$ has the advantage that it leads to a diffusion length ξ which is independent of the size s of the diffusing island (see below).

To obtain an expression for the capture number σ_{si} we consider [2] the diffusion equation for the local density n_s of clusters of size s, embedded in an average distribution of clusters, and diffusing toward a particular cluster of size i and radius r_i. Since the motion of island i will be taken into account in the capture number σ_{is}, we assume for simplicity that the island i is not moving. This leads to a local diffusion equation of the form

$$\frac{\partial n_s}{\partial\theta} = R_s\nabla^2 n_s + \mathcal{J}_s - R_s n_s/\xi_s^2, \qquad (6)$$

which is consistent with Eq. (3). Subtracting Eq. (3) from Eq. (6) gives

$$\frac{1}{R_s}\left(\frac{\partial n_s}{\partial\theta} - \frac{\partial N_s}{\partial\theta}\right) = \nabla^2 n_s - \xi_s^{-2}(n_s - N_s) \simeq 0. \qquad (7)$$

Assuming the boundary conditions $n_s(r_i) = 0$ (corresponding to irreversible growth) and $n_s(\infty) = N_s$, along with circular symmetry, leads to the solution

$$n_s(r) = N_s\left[1 - \frac{K_0(r/\xi_s)}{K_0(r_i/\xi_s)}\right]. \qquad (8)$$

From this, we obtain the following expression for the capture numbers

$$\sigma_{si} = \frac{2\pi r_i}{N_s}\left(\frac{\partial n_s}{\partial r}\right)_{r=r_i} = \frac{2\pi r_i}{\xi_s}\frac{K_1(r_i/\xi_s)}{K_0(r_i/\xi_s)}, \qquad (9)$$

where K_j is the modified Bessel function of order j. We note that for the case in which only monomers diffuse (e.g., $s = 1$, $\xi = \xi_1$) this result is consistent with the results of Bales and Chrzan [2].

We first consider the case $\Delta = 1$ which corresponds to an equal division of the aggregation term $2R_s\sigma_{ss}N_s^2$ [corresponding to the "capture" of a cluster of size s by another cluster of size s] between the two terms $\mathcal{J}_s$ and R_sN_s/ξ_s^2 of Eq. (3). We note that if the capture length ξ_s is independent of island size (e.g., $\xi_s = \xi$) then Eq. (9) implies that the capture number σ_{si} only depends on the size i of the "absorbing" island (e.g., $\sigma_{si} = \sigma_i$). For the case $\Delta = 1$, this is consistent with Eq. (5) which implies that $\xi_s = \xi$ for all s. Accordingly, our self-consistent RE approach corresponds to self-consistently solving the two equations

$$\frac{1}{\xi^2} = \sum_{i=1}^{\infty}\sigma_i N_i, \qquad (10a)$$

$$\sigma_i = \frac{2\pi r_i}{\xi}\frac{K_1(r_i/\xi)}{K_0(r_i/\xi)}, \qquad (10b)$$

as a function of the island densities $\{N_s\}$ at each integration step while the corresponding rate equations may be written

$$\frac{dN_s}{d\theta} = \delta_{s,1}\left(1 - \sum_{s=1}^{\infty}\kappa_i N_i\right) + \frac{1}{2}\sum_{i+j=s}(R_i\sigma_j + R_j\sigma_i)N_i N_j$$

$$- N_s\sum_{i=1}^{\infty}R_i\sigma_s N_i - R_s\sigma_s N_s^2. \tag{11}$$

While this approach is perhaps the most natural one, it is also interesting to consider the case $\Delta = 0$ since this corresponds to the Bales-Chrzan approach for the case in which only monomers diffuse. In this case, Eq. (5) becomes,

$$\frac{1}{\xi_s^2} = \sigma_{ss}N_s + \sum_{i=1}^{\infty}\sigma_{si}N_i, \tag{12}$$

and as a result the capture length ξ_s depends explicitly on s and is not consistent with the assumption ($\sigma_{si} = \sigma_i$) that the capture number depends only on the size of the "absorbing" cluster. Accordingly, to integrate the REs (1), the capture lengths ξ_s must be calculated self-consistently using Eqs. (9) and (12) at each integration step. Unfortunately, in addition to being computationally demanding, this approach leads to poor agreement with simulations except for the original case (studied by Bales and Chrzan [2]) in which only monomers diffuse and there is only one capture length ξ_1.

Accordingly, we have modified this approach by replacing the capture-length ξ_s in Eq. (3) and Eqs. (6)– (9), and (12) by a "renormalized" capture length ξ (averaged over all islands) defined by

$$\frac{\sum_{s=1}^{\infty}R_s N_s}{\xi^2} = \sum_{s=1}^{\infty}\frac{R_s N_s}{\xi_s^2}. \tag{13}$$

With this modification the capture numbers σ_i depend only on the size i of the "absorbing" island and Eq. (5) becomes

$$\frac{1}{\xi_s^2} = \sum_{i=1}^{\infty}\sigma_i N_i + (1 - \Delta)\sigma_s N_s. \tag{14}$$

Substituting this expression into the renormalization equation (13) the self-consistency condition becomes

$$\frac{1}{\xi^2} = \sum_{i=1}^{\infty}\sigma_i N_i + (1 - \Delta)\frac{\sum_{i=1}^{\infty}R_i\sigma_i N_i^2}{\sum_{i=1}^{\infty}R_i N_i}. \tag{15}$$

By solving Eqs. (10b) and (15) self-consistently, the rate-equations (11) may be numerically integrated for both $\Delta = 0$ and $\Delta = 1$. As previously noted, for the case in which only monomers diffuse, the assumption $\Delta = 0$ corresponds to the original equations of Bales and Chrzan.

III. MODEL AND SIMULATIONS

To test our self-consistent RE approach we have carried out KMC simulations of an off-lattice model of irreversible island growth in the presence of cluster diffusion. Since the details of this model have previously been described elsewhere [22], here we only describe it briefly. In our model we assume

that all islands are circular while irreversible aggregation and instantaneous relaxation are also assumed. In particular, each island or cluster of size s (where s is the number of monomers in a cluster) is represented by a circle with area $A_s = \pi d_s^2/4$ and diameter $d_s = d_1 s^{1/2}$, where d_1 is the monomer diameter. In addition, each cluster of size s may diffuse with diffusion rate $D_s = D_1 s^{-\mu}$ where $D_1 = D_{1,h}\delta^2/4$ is the monomer diffusion rate, $D_{1,h}$ is the monomer "hopping rate," and δ is the hopping length. Similarly, we may write $D_s = D_{s,h}\delta^2/4$ where $D_{s,h} = D_{1,h}s^{-\mu}$ is the hopping rate for a cluster of size s. In all of our simulations, we have assumed a hopping length $\delta = d_1$.

In order to take into account deposition, monomers are also randomly deposited onto the substrate with rate F/d_1^2 per unit time per unit area. Since instantaneous coalescence and relaxation are assumed, whenever two clusters touch or overlap, a new island is formed whose area is equal to the sum of the areas of the original clusters, and whose center corresponds to the center-of-mass of both islands. We note that in some cases a coalescence event may lead to the overlap of the resulting cluster with additional clusters. In this case, coalescence is allowed to proceed until there are no more overlaps. In addition, if a monomer lands on an existing cluster, then that monomer is automatically "absorbed" by the cluster.

Our simulations were carried out assuming a 2D square substrate of size L (in units of the monomer diameter d_1) and periodic boundary conditions. To avoid finite-size effects, the value of L used ($L = 4096$) was relatively large, while our results were averaged over 100 runs to obtain good statistics. To determine the asymptotic dependence of the island density on coverage and R_h our simulations were carried out using values of $R_h' = 4R_h/\pi$ ranging from 10^7–10^9 up to a maximum coverage of 0.1 monolayers (ML). To study the dependence on μ, simulations were carried out for $\mu = 1/2$ (corresponding to Brownian diffusion or uncorrelated evaporation-condensation), $\mu = 1$ (corresponding to correlated evaporation-condensation), and $\mu = 3/2$ (corresponding to periphery diffusion) as well as for higher values ($\mu = 2,3$, and 6) as well as the case $\mu = \infty$ corresponding to only monomer diffusion.

To obtain a quantitative understanding of the submonolayer growth behavior, we have measured a variety of quantities including the monomer density $N_1 = (\pi/4)n_1/L^2$ (where n_1 is the number of monomers in the system) as a function of coverage θ, and the average island density $N = (\pi/4)\sum_{s\geqslant 2}n_s(\theta)/L^2$ (where n_s is the total number of islands in the system). In addition, we have also measured the island-size distribution (ISD) $N_s(\theta)$ where $N_s = (\pi/4)n_s/L^2$ corresponds to the density of islands of size s (where s is the number of particles in the island) as well as the scaled ISD

$$f(s/S) = N_s(\theta)S^2/\theta, \tag{16}$$

where $S = (\theta - N_1)/N$ is the average island size. We note that the factors of $\pi/4$ in the definitions above take into account the fact that the area of a monomer is $(\pi/4)d_1^2$, and as a result the densities defined above all correspond to area fractions. Similarly, the coverage $\theta = \sum_{s\geqslant 1}sN_s$ corresponds to the fraction of the total area covered by islands (including monomers).

IV. RESULTS

In order to test our self-consistent RE approach, we have compared our RE results obtained using Eq. (15) for both $\Delta = 0$ and $\Delta = 1$ with simulation results for different values of μ. Somewhat surprisingly, we found that there was relatively little difference between our RE results for $\Delta = 0$ and those for $\Delta = 1$, although our $\Delta = 0$ results for the densities and ISDs were all in slightly better agreement with simulations than for $\Delta = 1$. Accordingly, the self-consistent RE results shown here correspond to this case. However, it should be noted that the difference between the results for both cases was typically less than 1%. For comparison, we have also carried out RE calculations using the mean-field (MF) Smoluchowski kernel appropriate in two-dimensions,

$$K_{ij}^{\mathrm{MF}} = \sigma_0 (D_i + D_j), \qquad (17)$$

where we have assumed $\sigma_0 = 1$ since this gives the best agreement with simulations.

A. Island and monomer densities

We first compare our self-consistent RE results for the evolution of the monomer density $N_1(\theta)$ and island density $N(\theta)$ with the corresponding simulation results for $R'_h = 10^7$ and 10^9. As shown in Fig. 1, for $\mu = 1/2$ and $\mu = 1$ there is good agreement between our KMC simulations (circles) and RE results (solid curves) up to and significantly beyond the coverage θ_{pk} corresponding to the peak island density. However, at a coverage ($\theta_c \simeq 0.02$) the RE predictions for the island density $N(\theta)$ begin to diverge somewhat from the KMC results, which decrease more rapidly with increasing coverage.

For comparison, RE results based on the Smoluchowski kernel $K_{ij} = \sigma_0 (D_i + D_j)$ with $\sigma_0 = 1$, corresponding to coverage- and size-independent capture number, are also shown. As can be seen, for $\mu = 1/2$ the agreement between the Smoluchowski RE results and simulations is as good as for our more complex self-consistent RE results, although neither approach correctly predicts the slight decrease in the island density beyond $\theta \simeq 0.02$. In contrast, for $\mu = 1$ our self-consistent RE results for the island density N are much closer to simulations than the constant capture-number results since they approximately predict the decrease of the island density beyond θ_{pk}. We note that for $R'_h = 10^9$ and $\mu = 1$, self-consistent RE results are not shown for coverage $\theta > 0.03$ due to the fact that the computation time becomes prohibitive.

Similar results are shown in Fig. 2 for $\mu = 3/2$ (corresponding to cluster diffusion via periphery diffusion) and $\mu = 2$. As can be seen, for both values of μ there is good agreement between our self-consistent RE results for the island density $N(\theta)$ and simulations all the way up to the maximum coverage $\theta = 0.1$. In contrast, the constant capture-number results lead to an island density which continues to increase beyond the peak-island coverage θ_{pk}, in disagreement with simulation results. Similarly, the self-consistent RE results for the monomer density $N_1(\theta)$ give significantly better agreement with simulations (for coverages up to the peak island density) than the constant capture-number results, although they predict
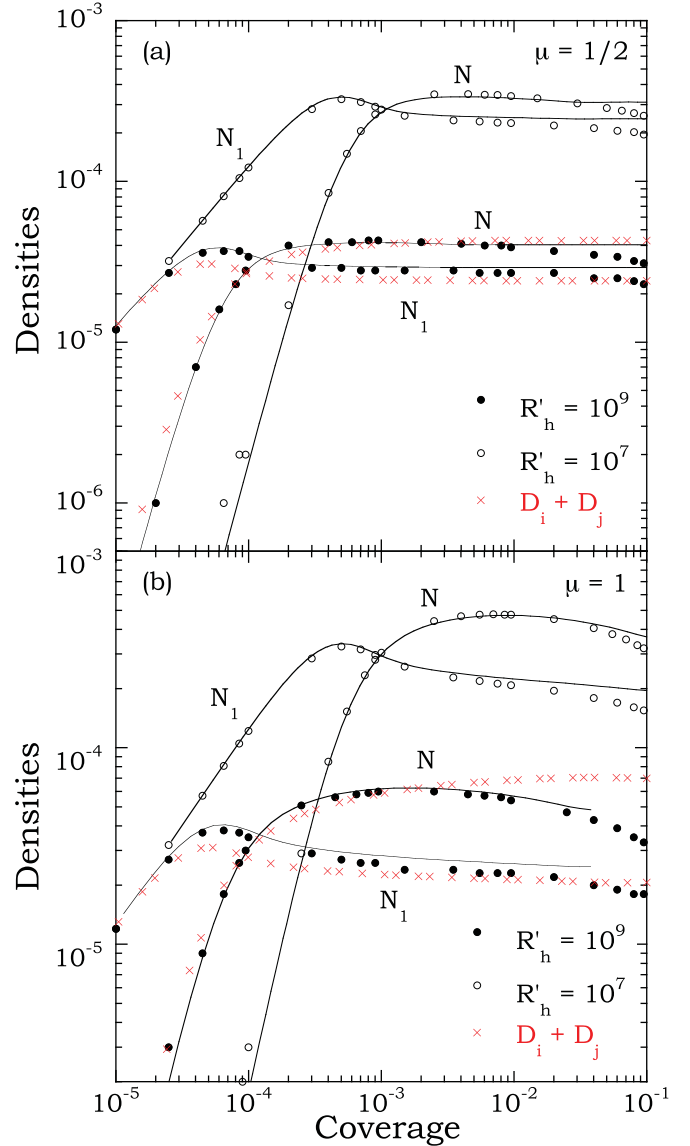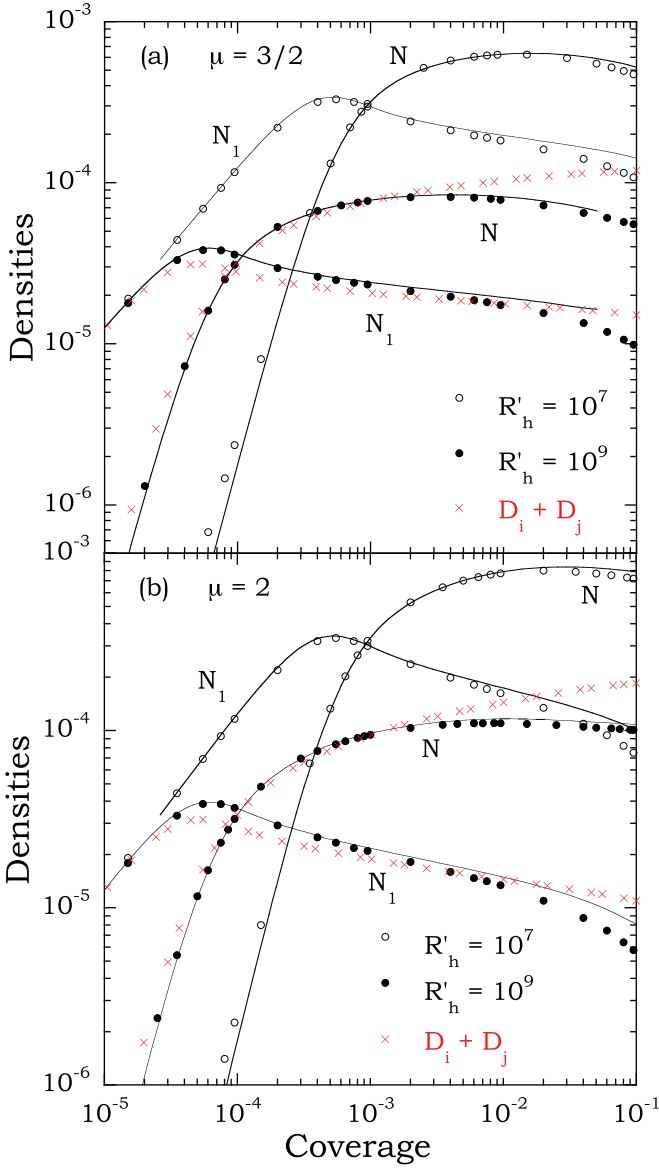

FIG. 1. (Color online) Comparison of self-consistent RE results (solid curves) with simulation results (circles) for the monomer density N_1 and island density N for $R'_h = 10^7$ and $R'_h = 10^9$ for (a) $\mu = 1/2$ and (b) $\mu = 1$. Also shown are constant capture-number results ($\times$) corresponding to $K_{ij} = D_i + D_j$.

a monomer density which decreases somewhat less rapidly beyond the peak coverage than the simulation results.

Results for $\mu = 3$ and $\mu = \infty$ are also shown in Fig. 3. We note that for these values of μ, the island density increases up to coverage $\theta = 0.1$. In this case, our self-consistent RE results for the island and monomer densities are in relatively good agreement with simulations although the RE results tend to be slightly higher. In contrast, the constant capture-number results give poor agreement with simulations.
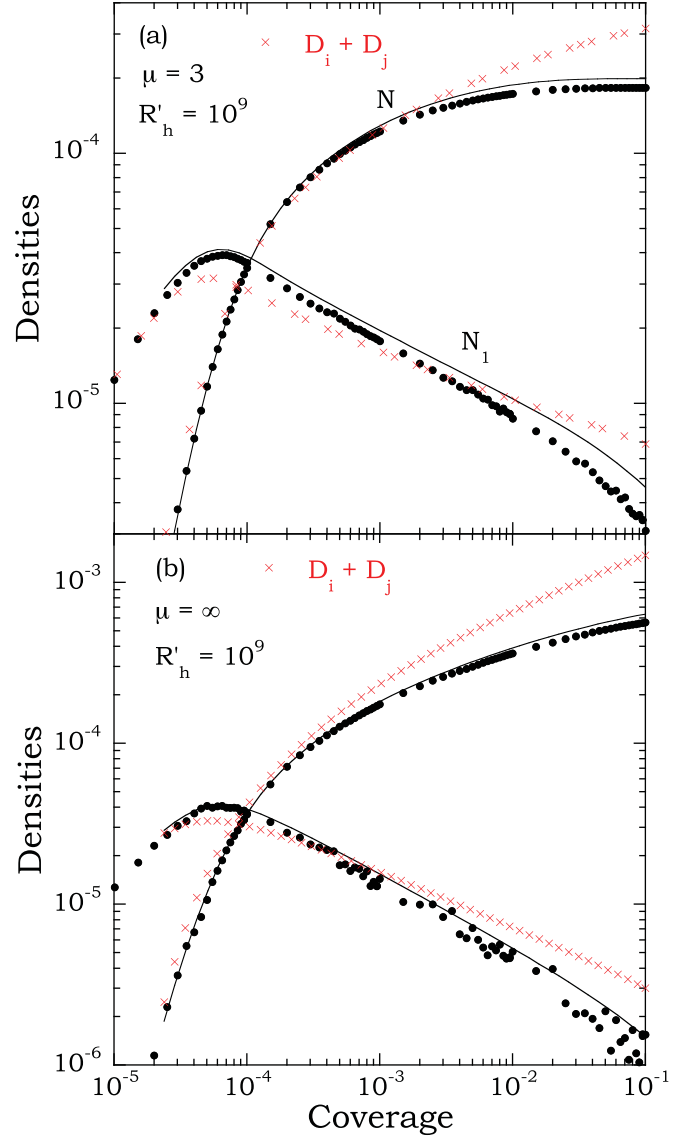
B. Island-size distribution

We now compare our self-consistent RE results for the scaled ISD with the corresponding simulation results at coverage $\theta = 0.01$ somewhat below the coverage corresponding to the peak island density. Figure 4 shows a comparison between

FIG. 2. (Color online) Same as Fig. 1. (a) $\mu = 3/2$ and (b) $\mu = 2$.

FIG. 3. (Color online) Same as Fig. 1. (a) $\mu = 3$ and (b) $\mu = \infty$.

our RE results for the scaled ISD (solid curve) and simulation results (filled symbols) at $\theta = 0.01$ for $\mu = 1/2$ and $\mu = 1$. As can be seen, for island sizes less than the average island size S there is excellent agreement with simulations. However, for $s > S$ (corresponding to large "ripe" islands for which correlations can develop) the agreement is not as good. For comparison, the RE results with constant capture number ($\sigma_0 = 1$) are also shown. While the constant capture number results agree with simulations for the very smallest island sizes, they disagree for larger island sizes.

We note that our ISD results for $\mu = 1/2$ are in qualitative agreement with the MF prediction [23–26] of power-law behavior $N_s \sim s^{-\tau}$ for $\mu < 1$. However, the value of the exponent [$\tau \simeq 1.35$, see Fig. 4(a)] obtained in our RE calculations and simulations is significantly higher than the value ($\tau = 1.25$) obtained using the MF prediction [23–26]

$$\tau = (3 - \mu)/2. \tag{18}$$

To further explore the dependence of τ on μ for $\mu < 1$, we have carried out additional simulations and RE calculations for both compact and point islands. As can be seen in Fig. 5, for the case of compact islands there is good agreement between our simulations and RE results for $\mu < 1$, while the exponent τ decreases approximately linearly[1] with increasing μ. Also shown in Fig. 5 are self-consistent RE results for the case of point islands corresponding to $r_s = r_1$. In contrast to our compact island results, these RE results are in good agreement with the MF prediction (18). This indicates that the deviations from the MF prediction for compact islands are not due to correlations (which are not included in our self-consistent RE approach), but rather to the effects of island geometry which are taken into account in our RE calculations.

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[1]Interestingly, for compact islands the exponent τ approximately satisfies the expression $\tau = (5 - 2\mu)/3$ rather than Eq. (18).
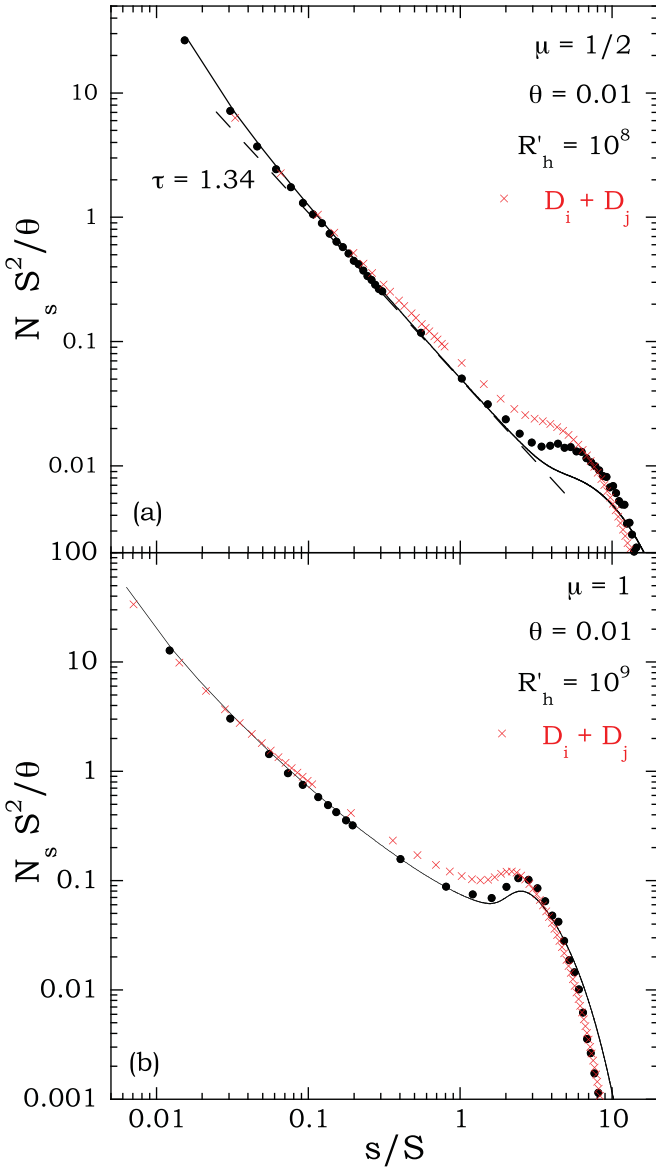
FIG. 4. (Color online) Comparison of self-consistent RE results (solid curves) with simulation results (circles) for the scaled ISD at $\theta = 0.01$ for (a) $\mu = 1/2$ and $R'_h = 10^8$ and (b) $\mu = 1$ and $R'_h = 10^9$. Also shown are constant capture number results (×) corresponding to $K_{ij} = D_i + D_j$.

Additional results for the scaled ISD for $\mu = 3/2$ and $\mu = 2$ are shown in Fig. 6. In both cases there is excellent agreement for all values of the scaled island size between our self-consistent RE results and simulations. In contrast, the constant capture number RE results exhibit poor agreement with simulations for small and intermediate island sizes. However, as shown in Fig. 7, for higher values of μ [e.g., $\mu = 3,6$ (not shown) and ∞], the height of the ISD peak at $s/S \simeq 1$ is significantly overestimated by our self-consistent RE approach, although there is still reasonable agreement with simulations for $s < S$. This behavior is similar to that previously found by Bales and Chrzan [2] for the case in which only monomers diffuse (corresponding to $\mu = \infty$) and is most likely due to the existence of correlations between the size of an island and its capture zone, which develop due to
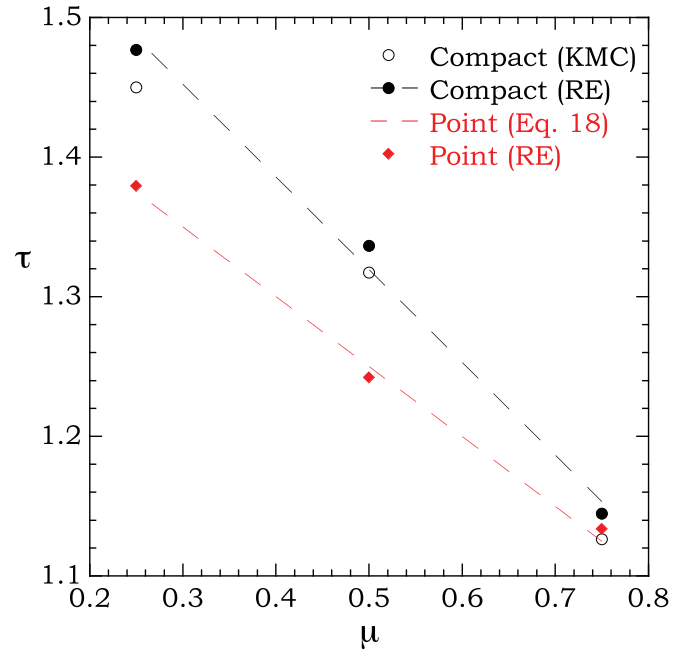

FIG. 5. (Color online) Simulation and self-consistent RE results for exponent τ for point islands (diamonds) and compact islands (circles) for $\mu = 1/4, 1/2, 3/4$ and $R'_h = 10^9$.

the decreased effects of cluster diffusion for large μ and large island sizes.

V. DISCUSSION

We have developed a self-consistent RE approach to irreversible island growth which takes into account cluster diffusion. In our approach, the capture length for an island of size s was assumed to be independent of its size, while the aggregation kernel K_{ij} was assumed to be equal to the sum of the capture rate $D_i \sigma_j$ of a cluster of size i by a stationary island of size j and the capture rate $D_j \sigma_i$ of a cluster of size j by a stationary island of size i. We note that while the radius of the capturing island is taken into account in our approach, the diffusing island is treated as a point-particle.[2] In this respect our approach is similar to that carried out by Bales and Chrzan [2] for the case in which only monomers diffuse.

In our approach we have considered two slightly different versions of our REs in which collisions between two islands of the same size are treated somewhat differently. In one method, corresponding to $\Delta = 0$ in Eq. (5), we have included the loss of both islands in the definition of the capture length. However, this leads to a size-dependent capture length as well as poor agreement with simulations. We have resolved this problem by renormalizing the capture length [see Eq. (15)] so that it is the same for all islands. Alternatively, for the case $\Delta = 1$, the loss of the "diffusing" island is assigned to the capture length [Eq. (5)] while the loss of the stationary island is assigned to the term $\mathcal{J}_s$ [Eq. (4)]. While such an approach is different

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[2]In contrast, directly taking into account the relative motion of two clusters of size i and j, as well as the sum $r_{ij} = r_i + r_j$ of their radii leads to poor agreement with simulations.
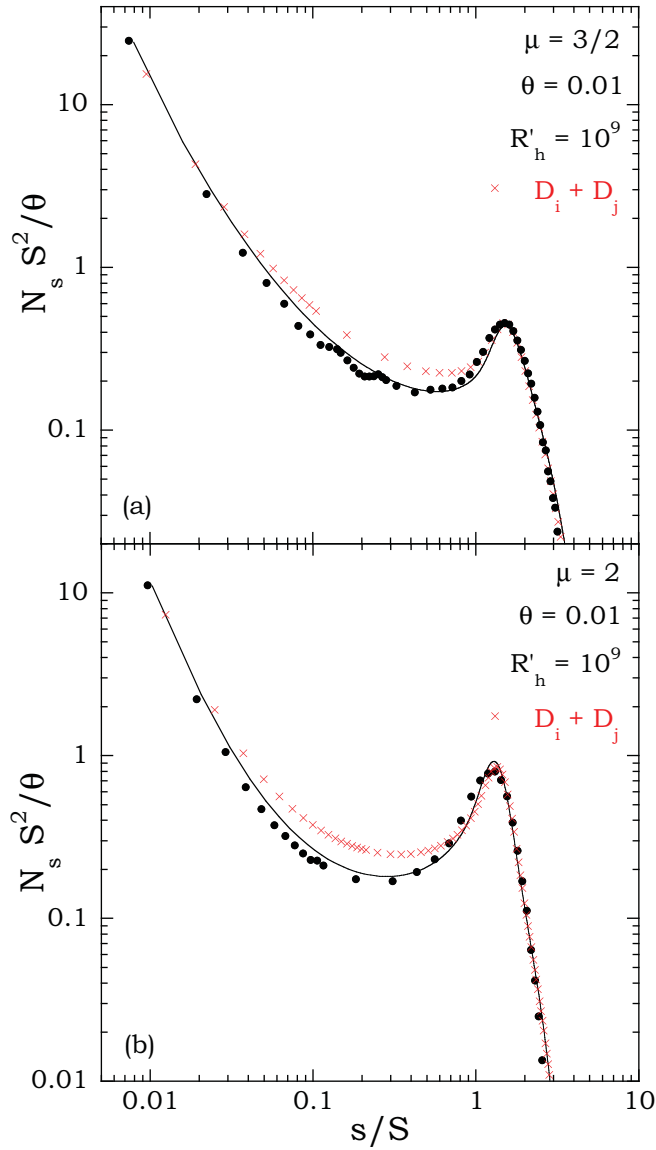
FIG. 6. (Color online) Comparison of self-consistent RE results (solid curves) with simulation results (circles) for the scaled ISD for $R'_h = 10^9$ and $\theta = 0.01$ for (a) $\mu = 3/2$ and (b) $\mu = 2$. Also shown are constant capture number results ($\times$) corresponding to $K_{ij} = D_i + D_j$.

FIG. 7. (Color online) Same as Fig. 6. (a) $\mu = 3$ and (b) $\mu = \infty$.

from that used by Bales and Chrzan [2] for the case in which only monomers diffuse, it automatically leads to a capture length which is independent of island size. In addition, in this case the results are very similar to those obtained for the case $\Delta = 0$. The relatively small difference between the results obtained using both approaches is most likely due to the fact that the "correction" term in Eq. (15) (which corresponds to the average value of $\sigma_i N_i$) is, in general, significantly smaller than the first term corresponding to $\sum_{i=1}^{\infty} \sigma_i N_i$.

As a first application of our self-consistent RE approach, we have applied it to a model of irreversible submonolayer growth in which the diffusion coefficient for an island of size s is given by $D_s = D_1 s^{-\mu}$. For all values of μ we find good agreement between our self-consistent RE results for the island and monomer densities and simulations, up to and
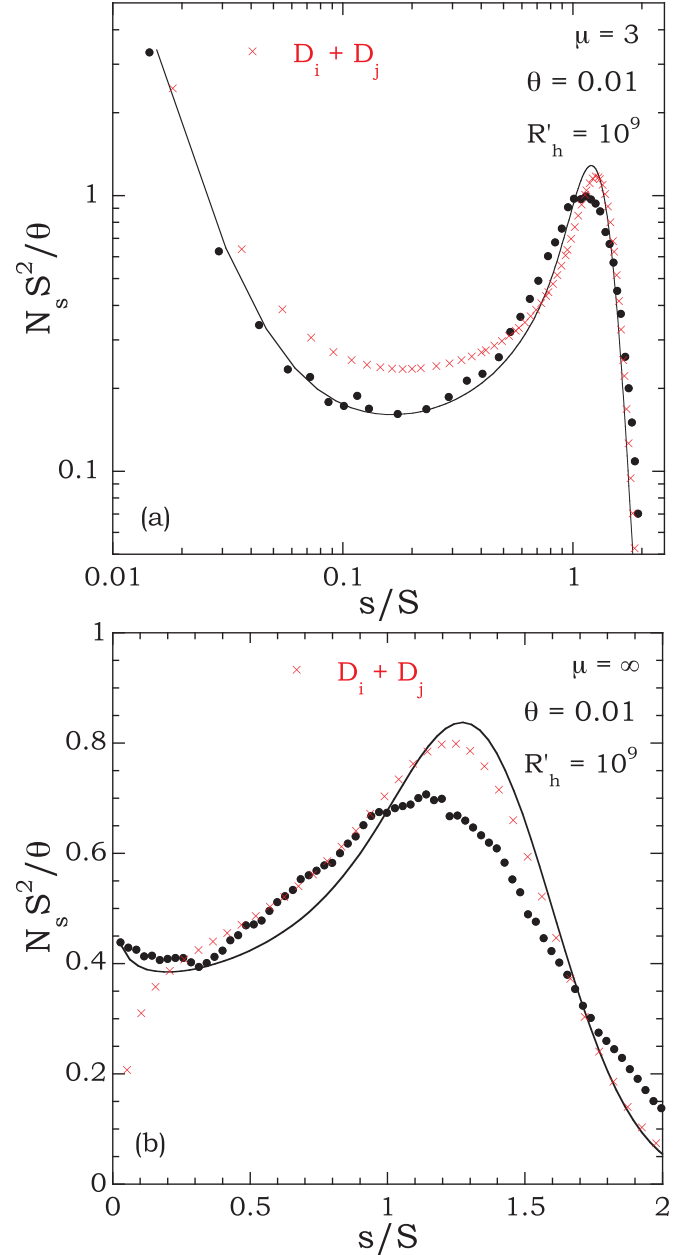
even somewhat beyond the coverage corresponding to the peak island density. Similarly, we have obtained good agreement for finite μ between our RE results and simulation results for the portion of the ISD corresponding to island sizes smaller than the average island size. We note that for $\mu < 3$ this corresponds to the dominant portion of the scaled ISD. Interestingly, for intermediate values of μ ($\mu = 3/2$ and 2) we also find excellent agreement between our ISD RE results and simulations for all values of the island size. This result is perhaps not so surprising since one of the motivations of this work was our expectation that the presence of significant cluster mobility for large islands would reduce the effects of correlations and thus lead to improved prediction of the ISD. However, for $\mu \geqslant 3$ the effects of correlations become important for large islands and as a result the agreement decreases with increasing μ.

We have also compared our results with those obtained using the MF Smoluchowski expression (17) corresponding to constant and size-independent capture numbers. In general, we find that, except for the case $\mu = 1/2$ (for which the island and monomer densities are reasonably well predicted) such an approach leads to results which are in poor agreement with simulations. In addition, we find that even for $\mu < 1$ (for which power-law behavior of the ISD is expected) our self-consistent RE results are in good agreement with simulation results even though the measured value of τ differs from the MF Smoluchowski prediction Eq. (18).

Since our REs do not take into account correlations, this implies that the size dependence of the ISD for $\mu < 1$ can be explained almost entirely by geometric effects which are taken into account in our self-consistent RE approach. This is further confirmed by the fact that our self-consistent RE results for point islands are in good agreement with the MF prediction Eq. (18) for $\tau(\mu)$. These results indicate that even for the case $\mu < 1$, for islands with a realistic geometry in two dimensions, the self-consistent RE approach developed here is preferable to the MF Smoluchowski approach.

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