Dynamics of first-order phase transitions: Theory of coarsening (Ostwald ripening) for open systems

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Late-stage diffusion-controlled coarsening during the process of phase separation is considered. We derive a reduced theory in terms of ordinary differential equations for the cluster density, mean cluster size, width of the cluster size distribution, and supersaturation. Parameters introduced by the approximations are fixed such as to yield agreement with the asymptotic Lifshitz-Slyozov-Wagner theory. The theory improves upon the work of Langer and Schwartz because it includes subcritical clusters as part of the minority phase and explicitly considers the width of the size distribution which controls the rate of coarsening. The theory is constructed in a way which allows treating open systems. For a two-cell model with diffusional coupling we numerically solve the full equation for the size distribution and prove the quality of our theory through the comparison. In addition, we propose an approximate procedure to include the effect of a finite volume fraction of the minority phase and the process of coagulation.

I. INTRODUCTION

A complete theory of the dynamics of first-order phase transitions would have to account for a variety of physical processes on different time and length scales including nucleation, spinodal decomposition, growth of clusters of the minority phase in the two-phase region, and late-stage coarsening processes like Ostwald ripening and coagulation (see Ref. 1 for a recent review). Up until now theories generally have to be confined to certain aspects of the total dynamics extending from an initial quench to the establishment of full phase separation.

This work is concerned with the late-stage coarsening process when, driven by their surface-to-volume ratio, larger clusters of the minority phase grow at the expense of the smaller ones. This process, called Ostwald ripening, results in a substantial increase of the average cluster size and a corresponding decrease of their number density. Depending on the kinetics of cluster growth of course, the process may last extremely long times if other effects do not interfere.

The theory of Ostwald ripening goes back to the pioneering work of Lifshitz and Slyozov[2] and, independently, Wagner.[3] They describe the heterogeneous system in the two-phase region within the droplet model using a cluster size distribution which changes due to monomer condensation and/or evaporation in solution. Their theory applies to closed systems with conservation of matter and provided evidence for the existence of a universal distribution function if appropriately scaled variables are used and for universal power laws in time for the physical quantities like cluster density and mean cluster size. Universality here means asymptotic ($t \to \infty$) independence of initial conditions. Of course, the universal distribution function as well as the exponents of the power laws depend on the kinetics of cluster growth.

Recently, in a paper on the theory of completion time for near-critical systems Langer and Schwartz[4] presented an approximate theory in terms of ordinary differential equations for the cluster density, the average cluster size, and the monomer concentration. Their approximations introduce certain parameters which are chosen such that the asymptotical evolution agrees with the more complete theory in terms of the full droplet distribution function. Since Langer and Schwartz need a theory which describes nucleation *and* coarsening they choose to count only overcritical particles as part of the minority phase. This is necessary in order to cope with the bimodality of the cluster distribution function at early times after the quench when nucleation is non-negligible. At late times, however, the distribution function is essentially unimodal and the cluster distribution consists of overcritical (growing) particles and undercritical (dissolving) particles which both contain comparable volume of the minority phase.

Since our theory is intended only to describe late-stage coarsening processes when nucleation can be neglected we need not make the restricting assumption of Langer and Schwartz. Otherwise our theory is similar in spirit to theirs. We consider an additional dynamical variable, namely the width of the cluster distribution which controls the aging rate. Equations of motion are derived for the limit of a narrow distribution function. The expansion parameter is the relative width squared which is roughly $\frac{1}{3}$ asymptotically. Since particles are confined to have positive size a certain limit of the distribution function for vanishing size is involved in the theory. It is parametrized in a physically plausible way as a function of the dynamical variables considered explicitly. Parameters are chosen such as to render the asymptotics in accord with the theory of Lifshitz and Slyozov.

Our theory is formulated in a way which allows the treatment of open systems. Examples are external variations of the temperature or monomer flux across the boundary of the system. This is motivated by research on macroscopic pattern formation during the precipitation of weakly soluble salts ("Liesegang phenomenon").[5,6] Here a

pattern develops with a length scale L which is large compared to the mean particle distance $n^{-1/3}$. An explanation which has been proposed considers competitive coarsening mediated by monomer diffusion over macroscopic distances.[6(b),7-11] A satisfying theory along this line of thought should consider mesoscopic regions of a length scale l with $L \gg l \gg n^{-1/3}$. These mesoscopic regions undergo "local" coarsening because of Ostwald ripening but are necessarily open to flux of monomer. Previous theories, except for Ref. 10, have neglected the influence of local coarsening completely.

Section II of this paper describes the derivation of our theory. In order to evaluate the quality of its predictions we apply it to the idealized model of competitive coarsening between two homogeneous systems ("cells") coupled by monomer exchange. In this case the numerical solution of the complete theory in terms of the full cluster distribution is readily possible and serves as a means for comparison. The approximate theory proves to be fairly accurate in spite of the crude approximations involved. This will be described in Sec. III. Our theory was developed for a particle growth law valid in the limit of zero volume fraction φ of the minority phase. Recent work[11,12] has shown that a finite φ produces a correction proportional to $\varphi^{1/2}$ to the particle growth law as well as an additional collision term and nonthermal fluctuations. In Sec. IV we propose an approximate way to include the renormalization of the growth law. In addition, we show how coagulation may be accounted for within our theory and furthermore discuss the stability of the symmetric state of the two-cell model used in Sec. III.

II. THEORY

We consider the time evolution of an ensemble of particles of the minority phase distributed in the bulk of the majority phase. The latter is described as a solution of monomers which are the constituents of the minority phase. Within the traditional droplet model the system is completely characterized by the particle size distribution function $f(r,t)$, where r is the radius of an individual particle of the ensemble, and the average monomer concentration $\bar{c}(t)$ in solution. The distribution function $f(r,t)$ is normalized to the total particle density $n(t) = \int_0^\infty dr\, f(r,t)$. Instead of the monomer concentration one conveniently uses the supersaturation ratio $\sigma(t)=[\bar{c}(t)-c_{eq}(\infty)]/c_{eq}(\infty)$ where the concentration $c_{eq}(\infty)$ which is in equilibrium with an infinitely large particle of the minority phase has been introduced.

Since we are interested in the late-stage evolution of the system when $\sigma(t)$ is small, the creation of new particles because of nucleation events is negligible. In addition we shall neglect coagulation and the reverse process of splitting of particles into smaller ones for the moment. Then the particle size distribution will change due to monomer condensation and/or evaporation only. If we denote the growth rate of a particle of radius r in the presence of supersaturation σ by $\dot{r}=V(r,\sigma)$ the distribution function $f(r,t)$ fulfills the continuity equation

$$\frac{\partial}{\partial t}f(r,t)+\frac{\partial}{\partial r}V(r,\sigma)f(r,t)=0 . \tag{1}$$

Conservation of matter implies

$$\sigma(t)+\frac{4\pi}{3vc_{eq}(\infty)}\int_0^\infty dr\, r^3 f(r,t)=q(t) . \tag{2}$$

The volume per monomer in the minority phase and the total amount of matter in terms of supersaturation are denoted by v and $q(t)$, respectively. For a closed system the latter may be expressed as $q=[\bar{c}_{in}-c_{eq}(\infty)]/c_{eq}(\infty)$ where $\bar{c}_{in}$ is the initial concentration of monomer immediately after the quench but before nucleation has started. In general, q may be time dependent if exchange of matter with the environment, e.g., by diffusion of monomer across the boundaries of the system, is possible or if $c_{eq}(\infty)$ depends on time, e.g., via its temperature dependence.

In addition to the time dependence of q, we have to specify the particle growth law $V(r,\sigma)$. We consider the limit of sufficiently fast interface kinetics such that the growth is limited by the diffusion of monomer towards the particles. The traditional growth law for this case is[2,13]

$$V(r,\sigma)=\frac{Dvc_{eq}(\infty)}{r}(\sigma-\alpha/r) . \tag{3}$$

D and α are the monomer diffusion coefficient and a capillarity length, respectively. The growth law (3) results from the stationary solution for the diffusion field around a single spherical particle of radius r subject to the boundary conditions $c_{eq}(r)\approx c_{eq}(\infty)(1+\alpha/r)$ at the particle surface and $\bar{c}$ at infinite distance from the particle. The perturbation of the homogeneous concentration $\bar{c}$ turns out to be long ranged with a dependence on distance like a Coulomb potential. Nevertheless, the growth law (3) neglects the interaction of the diffusion fields of neighboring particles in the ensemble. This is justified in the limit of vanishing volume fraction of the minority phase. Recent work has shown that corrections to (3) and the continuity equation (1) are proportional to the square root of the volume fraction.[11,12] We neglect these corrections for the bulk of this paper but an approximate way to incorporate them into our theory is proposed in the discussion (Sec. IV).

In what follows we first perform a reformulation of the given set of equations without any further approximations. In order to improve the transparency of the presentation we do this in two steps. First, it is convenient to measure the particle radius in units of the critical radius $r_c(t)=\alpha/\sigma(t)$ which is in equilibrium with a solution of supersaturation $\sigma(t)$. In addition, we characterize the particles by their volume instead of their radius and introduce the variable

$$z=[\sigma(t)r/\alpha]^3 . \tag{4}$$

The corresponding distribution function $F(z,t)$ which is still normalized to the particle density fulfills

$$\frac{\partial}{\partial t}F(z,t)+3\sigma^3(t)\frac{\partial}{\partial z}\left[\lambda(z^{1/3}-1)+\frac{\dot{\sigma}(t)}{\sigma^4(t)}z\right]F(z,t)=0 . \tag{5}$$

Conservation of matter is expressed as

$$\sigma(t)+[n_0\sigma^3(t)]^{-1}\int_0^\infty dz\, zF(z,t)=q(t)\ . \tag{6}$$

We have introduced the rate constant

$$\lambda=Dvc_{\rm eq}(\infty)/\alpha^2 \tag{7}$$

and a particle density

$$n_0=\frac{3vc_{\rm eq}(\infty)}{4\pi\alpha^3} \tag{8}$$

which for typical values of the material constants are about $10^4\ {\rm s}^{-1}$ and $10^{15}\ {\rm cm}^{-3}$, respectively.[14] Note that due to the time dependence of the critical radius an additional drift term proportional to the time derivative of the supersaturation appears in Eq. (5).

As the second step in our reformulation we introduce a distribution function $\phi(z,t)$ which is normalized to unity. This is motivated by the existence of the asymptotic regime for closed systems characterized by

$$F(z,t)\longrightarrow n(t)\phi(z,\infty),\quad \text{as } t\longrightarrow\infty\ . \tag{9}$$

The asymptotic time dependence of the particle density $n(t)$ as well as the shape of the normalized distribution $\phi(z,\infty)$ are the result of the Lifshitz-Slyozov-Wagner theory.[2,3] Recently, asymptotic corrections to (9) have been calculated by analytic means.[15] In a numerical study the evolution of $F(z,t)$ and $\sigma(t)$ has been investigated for various initial conditions and the existence of an asymptotic regime has been demonstrated explicitly.[16]

We define the normalized distribution function

$$\phi(z,t)=F(z,t)\Big/\int_0^\infty dz\, F(z,t) \tag{10}$$

and obtain the following set of equations:

$$\dot n(t)=-3\lambda\sigma^3(t)n(t)\phi(0,t)\ , \tag{11}$$

$$\frac{\partial}{\partial t}\phi(z,t)+3\lambda\sigma^3(t)\frac{\partial}{\partial z}\left[\lambda(z^{1/3}-1)+\frac{\dot\sigma(t)}{\sigma^4(t)}z\right]\phi(z,t)$$
$$=3\lambda\sigma^3(t)\phi(0,t)\phi(z,t)\ , \tag{12}$$

$$\sigma(t)+\frac{n(t)}{n_0\sigma^3(t)}\langle z\rangle=q(t)\ . \tag{13}$$

Equation (13) contains the expectation value $\langle z\rangle$ which is defined according to the prescription

$$\langle\cdots\rangle=\int_0^\infty dz\,(\cdots)\phi(z,t)\ . \tag{14}$$

For further use we note the differential form of (13),

$$\dot\sigma(t)=\dot q(t)-3\lambda\frac{n(t)}{n_0}\langle z^{1/3}-1\rangle\ . \tag{15}$$

This completes our formal manipulations which transformed the original set of equations (1)–(3) into Eqs. (11)–(13). Before proceeding towards an approximate reduced theory we shall demonstrate that the transformed set of equations without any involved analysis predicts the correct asymptotic behavior for closed systems if only one constant is fixed appropriately.

For a closed system at constant temperature we have $\dot q=0$ and asymptotically $\sigma(t)\ll q$. Using Eqs. (13) and (15) this implies

$$\dot\sigma(t)\approx-3\lambda q\sigma^3(t)\frac{\langle z^{1/3}-1\rangle}{\langle z\rangle}\ . \tag{16}$$

From Eq. (12) one readily calculates the time derivative of the first moment of $\phi(z,t)$,

$$\langle\dot z\rangle=3\lambda\sigma^3(t)[\langle z^{1/3}-1\rangle+\phi(0,t)\langle z\rangle]+3\frac{\dot\sigma(t)}{\sigma(t)}\langle z\rangle \tag{17}$$

which by means of (16) becomes in the same limit $\sigma(t)\ll q$

$$\langle\dot z\rangle\approx-9\lambda q\sigma^2(t)\langle z^{1/3}-1\rangle+3\lambda\sigma^3(t)\phi(0,t)\langle z\rangle\ . \tag{18}$$

If an asymptotic distribution $\phi(z,\infty)$ with a certain first moment $\langle z\rangle_\infty$ exists this implies

$$\langle z^{1/3}-1\rangle\approx\frac{\sigma(t)}{3q}\phi(0,\infty)\langle z\rangle_\infty \tag{19}$$

and, again using (16),

$$\dot\sigma(t)\approx-\lambda\phi(0,\infty)\sigma^4(t)\ . \tag{20}$$

The differential equation can be integrated to yield

$$\sigma(t)\approx[3\lambda\phi(0,\infty)t]^{-1/3} \tag{21}$$

which agrees with the asymptotic result of the Lifshitz-Slyozov-Wagner theory if we choose $\phi(0,\infty)=\frac{4}{27}$. The time dependence of the particle density $n(t)$ follows from (21) and the conservation law (13) but needs additional knowledge of $\langle z\rangle_\infty$.

We continue our general discussion and derive the time derivative of the expectation value $\langle z^\gamma\rangle$ for a positive γ which needs not necessarily be integer. The result is

$$\langle\dot z^\gamma\rangle=3\gamma\lambda\sigma^3(t)\langle z^{\gamma-1}(z^{1/3}-1)\rangle$$
$$+3\gamma\frac{\dot\sigma(t)}{\sigma(t)}\langle z^\gamma\rangle+3\lambda\sigma^3(t)\phi(0,t)\langle z^\gamma\rangle\ . \tag{22}$$

The derivation involves a partial integration which yields vanishing boundary terms at $z=0$ only if γ is positive. At first sight it might seem that Eq. (22) constitutes a hierarchy of coupled equations since a moment of order γ is coupled to moments of order $\gamma-\frac{2}{3}$ and $\gamma-1$. However, starting with a certain γ there is no way to escape the appearance of moments with negative exponents through the application of (22) which in turn ceases to be applicable. The deeper reason for this is the nonanalytic behavior of the drift term in (12) for $z\longrightarrow0$ which stems from the singularity of $V(r,\sigma)$, Eq. (3), for $r\longrightarrow0$.

The difficulties with the hierarchy of moments can be avoided if one uses cumulants and expands the expectation values of noninteger powers of z in terms of the cumulants. In this paper we only consider the second cumulant $K_2=\langle z^2\rangle-\langle z\rangle^2$ and assume cumulants of order 3 and higher to be negligible. It is straightforward to improve on this. However, even this crude approximation turns out to yield satisfying results in comparison with numerical solutions of the full partial differential equations (see Sec. III). From (22) one derives

$$\dot K_2=6\lambda\sigma^3(t)[\langle z^{4/3}\rangle-\langle z\rangle\langle z^{1/3}\rangle]+6\frac{\dot\sigma(t)}{\sigma(t)}K_2$$
$$+3\lambda\sigma^3(t)\phi(0,t)(K_2-\langle z\rangle^2)\ . \tag{23}$$

Expectation values $\langle z^\gamma \rangle$ are approximated in the following way:

$$\langle z^\gamma \rangle = \langle z \rangle^\gamma \left\langle \left[1+\frac{\delta z}{\langle z \rangle} \right]^\gamma \right\rangle \approx \langle z \rangle^\gamma \left[1+\frac{\gamma(\gamma-1)}{2}\frac{K_2}{\langle z \rangle^2} \right], \tag{24}$$

where δz denotes $z-\langle z \rangle$. Obviously one has $\langle \delta z \rangle = 0$ and $\langle \delta z^2 \rangle = K_2$. It is convenient to use a normalized second cumulant

$$x = K_2/\langle z \rangle^2 . \tag{25}$$

Note that x plays the role of an expansion parameter in Eq (24). The equations of motion for $\langle z \rangle$, x, and σ become approximately

$$\dot{\langle z \rangle} \approx 3\lambda\sigma^3(t) \left[\left[1-\frac{x}{9} \right] \langle z \rangle^{1/3} - 1 + \phi(0,t)\langle z \rangle \right] + 3\frac{\dot{\sigma}(t)}{\sigma(t)}\langle z \rangle , \tag{26}$$

$$\dot{x} \approx \lambda\sigma^3(t) \left[2x\langle z \rangle^{-2/3} \left[\frac{x}{3} - 2 + 3\langle z \rangle^{-1/3} \right] - 3(1+x)\phi(0,t) \right] , \tag{27}$$

$$\dot{\sigma} \approx \dot{q} - 3\lambda\frac{n(t)}{n_0} \left[\left[1-\frac{x}{9} \right] \langle z \rangle^{1/3} - 1 \right] . \tag{28}$$

The equation for $n(t)$, Eq. (11), remains unaffected by these approximations.

In order to have a closed system of ordinary differential equations we have to specify the boundary value $\phi(0,t)$ suitably. We assume that it is only determined by the actual values of $\langle z \rangle$ and x. In Appendix A we give an argument that, in the limit of small x, a reasonable functional form of $\phi(0,t)$ should read

$$\phi(0,t) = \frac{\beta(x)}{\langle z \rangle} , \tag{29}$$

where $\beta(x)$ is an increasing function of x. This form agrees with our intuitive expectation about the dependence of $\phi(0,t)$ on the average value $\langle z \rangle$ and the width of the distribution which we denote by $\Delta z = K_2^{1/2} = (x\langle z \rangle)^{1/2}$. In terms of $\langle z \rangle$ and Δz Eq. (29) reads

$$\phi(0,t) = \langle z \rangle^{-1}\beta[(\Delta z/\langle z \rangle)^2] . \tag{29'}$$

$\phi(0,t)$ decreases if $\langle z \rangle$ increases for fixed Δz but increases if Δz increases with $\langle z \rangle$ fixed, both in agreement with our expectation. In addition we assume a power-law dependence of $\beta(x)$ on x, i.e.,

$$\phi(0,t) = \beta_0 x^p/\langle z \rangle . \tag{30}$$

It turns out that β_0 and the exponent p in (30) are not independent parameters if one prescribes the asymptotic time dependence of the supersaturation $\sigma(t)$ in accord with the Lifshitz-Slyozov-Wagner theory. This imposes $\phi(0,\infty) = \frac{4}{27}$, cf. Eq. (21) and the discussion thereafter. One obtains

$$\beta_0 = \tfrac{4}{27}\langle z \rangle_\infty x_\infty^{-p} . \tag{31}$$

The asymptotic values $\langle z \rangle_\infty$ and x_∞ are given by the (physical) stationary point of Eqs. (26) and (27) in the limit $\sigma(t) \ll q$. Their magnitudes are $\langle z \rangle_\infty \approx 1.112$ and $x_\infty \approx 0.313$. The agreement with the corresponding quantities for the asymptotic distribution of the Lifshitz-Slyozov-Wagner theory is excellent for $\langle z \rangle_\infty$ ($\langle z \rangle_\infty^{\mathrm{LSW}} \approx 1.130$) and reasonable for x_∞ ($x_\infty^{\mathrm{LSW}} \approx 0.261$). An additional restriction on p is provided by the demand that the asymptotic stationary point of Eqs. (26) and (27) be stable. This yields an inequality $p > p_{\min}$ with $p_{\min}$ somewhat larger than unity. Details of these considerations may be found in Appendix B.

Let us briefly summarize the main result of this section. We have derived an approximate theory of coarsening in terms of coupled ordinary differential equations for the particle density $n(t)$, the average particle size $\langle z \rangle$ in terms of the volume of the critical particle, the relative width x of the distribution function, and the supersaturation $\sigma(t)$. The corresponding equations are (11), (26), (27), and (28), respectively, supplemented by Eq. (30) for $\phi(0,t)$. The theory contains one parameter, say the exponent p in (30). Because of the presence of the term $\dot{q}(t)$ in Eq. (28) it is in principle applicable to open systems. In order to test the quality of the theory we shall compare its predictions with numerical solutions of the full partial differential equation.

III. COMPARISON WITH EXACT SOLUTIONS

In Sec. II an approximate theory was derived for coarsening (Ostwald ripening) in the limit of vanishing volume fraction of the minority phase and for diffusion-controlled particle growth. Our starting point was a formulation in terms of the particle size distribution $f(r,t)$ as given by Eqs. (1)–(3). Despite the fact that this description necessarily involves certain approximations it will be termed the "exact" theory against which our approximate theory has to be compared.

In a recent publication[10] we have presented numerical solutions of the exact theory for closed systems. The same method can be applied to open systems where the total amount of matter $q(t)$, cf. Eq. (2) or (13), is not constant. Instead of prescribing a certain time dependence of $q(t)$, however, we found it more interesting to study the following idealized situation depicted schematically in Fig. 1. Two spatially homogeneous systems described by size distributions $f_i(r,t)$ and supersaturations $\sigma_i(t)$ with $i=1,2$ are open with respect to monomer exchange across their mutual boundary. The idealization is that diffusional relaxation within the cells is quick enough so that the concentrations can be assumed spatially constant. The rate of monomer exchange is modeled proportional to the concentration difference $\sigma_1(t)-\sigma_2(t)$. Since the total system is assumed to be closed we have

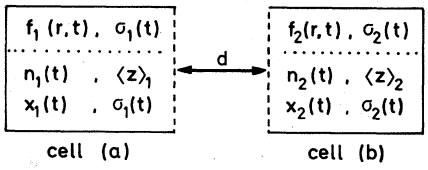

FIG. 1. Schematic representation of the two-cell model with diffusional coupling (coupling constant d). Within the boxes the level of description is indicated for the exact theory (upper part) and the approximate theory (lower part).

$$\dot{q}_1(t)=\lambda d[\sigma_2(t)-\sigma_1(t)] ,$$
$$\dot{q}_2(t)=\lambda d[\sigma_1(t)-\sigma_2(t)] . \tag{32}$$

The rate constant λ is given by (7). The parameter d measures the dimensionless strength of diffusional interaction.

In order to perform the numerical solution of the exact theory we have to specify initial conditions. For the normalized distributions $\phi_i(z,t)$ we use

$$\phi_i(z,0)=Y_i(z)\Big/\int_0^\infty dz\, Y_i(z) \tag{33}$$

with

$$Y_i(z)=\exp\left[z^{1/3}+\tfrac{1}{2}z^{2/3}-\frac{1}{2}\left[\frac{z-z_m^{(i)}}{\Delta z^{(i)}}\right]^2\right] . \tag{34}$$

This functional form has the property that the singularity of the derivative of the drift term in Eq. (12) for $z\to 0$ is compensated for by an appropriate singularity of the derivative of $\phi(z,0)$. The parameters $z_m^{(i)}$ and $\Delta z^{(i)}$ control the average size $\langle z\rangle_i$ and the width x_i of the initial distribution. For the calculations to be reported we chose $z_m^{(i)}=\Delta z^{(i)}=1$ for both subsystems. As the initial supersaturations we chose $\sigma_1(0)=0.25$ and $\sigma_2(0)=0.50$. The initial particle densities were fixed such that the total amount of matter is unity in both subsystems initially. This implies $n_i(0)=n_0\sigma_i^3(0)[1-\sigma_i(0)]/\langle z\rangle_i(t=0)$ where $\langle z\rangle_i(t=0)$ is the average calculated from $\phi_i(z,0)$, Eq. (33).

The numerical solution of the approximate theory derived in Sec. II is straightforward since only ordinary differential equations are involved. The initial values are $\sigma_i(0)$ and $n_i(0)$ as given above and the mean value $\langle z\rangle_i(t=0)$ and the relative width $x_i(0)$ as calculated from $\phi_i(z,0)$. The numerical values are $\langle z\rangle_i(t=0)=1.678$ and $x_i(0)=0.249$. The remaining parameter, namely the exponent p in Eq. (30), was chosen $p=3$ for the results to be shown in the figures. The dependence on the precise value of p is weak. Figures 2–12 are selected graphs depicting solutions of the approximate theory (full curves) in comparison with exact results (broken lines). The two subsystems are labeled a ($i=1$) and b ($i=2$).

Let us first discuss the time evolution for closed systems. This is realized if the diffusional coupling constant d is zero. The subsystems are closed systems with different initial conditions. Figures 2 and 3 show the mean particle size $\langle z\rangle$ and the relative width $x=\langle(z-\langle z\rangle)^2\rangle/\langle z\rangle^2$ as a function of the dimensionless time $\tau=t/T$ where $T=1/\lambda$ is a typical time scale of the system. One realizes an initial time regime up to $\tau\approx 10^2$ during which the average $\langle z\rangle$ relaxes towards its asymptotic value and the width x approaches a magnitude which is the asymptotic value for the approximate theory (solid lines) but an intermediate value for the exact theory. The reorganization of the shape of the distribution function which occurs for $\tau>10^2$ is not contained in our theory and shows its shortcomings. Probably the agreement will improve if higher cumulants are included. We note in passing that the evolution of $n(t)$ and $\sigma(t)$ is virtually identical for both theories in a double-logarithmic plot.

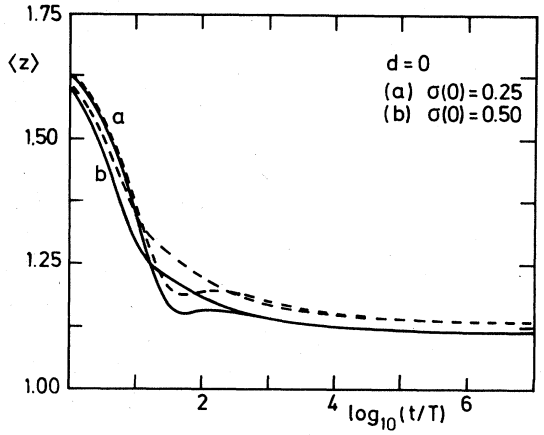

FIG. 2. Mean particle size for two uncoupled systems (labels a and b) with different initial conditions (see inset and text) as a function of the reduced time $\tau=t/T$. Solid lines, approximate theory; dashed lines, exact theory.

Next we consider coupled systems with a small coupling constant $d=0.01$. Figures 4, 5, 6 and 7 show the evolution of $n_i(t)$, $\langle z\rangle_i(t)$, $x_i(t)$, and $q_i(t)$, respectively. Physically, subsystem b ($i=2$) has a higher initial mono-

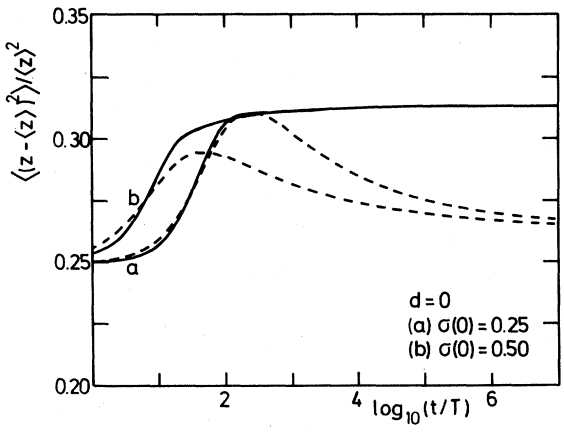

FIG. 3. Relative width of the distribution function as a function of time. Same conditions as Fig. 2.

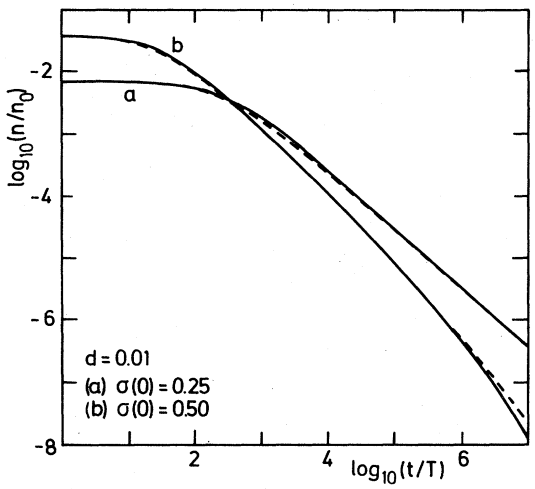

FIG. 4. Particle density for coupled cells ($d=0.01$) with different initial conditions (see inset) as a function of time. Solid lines, approximate theory; dashed lines, exact theory.

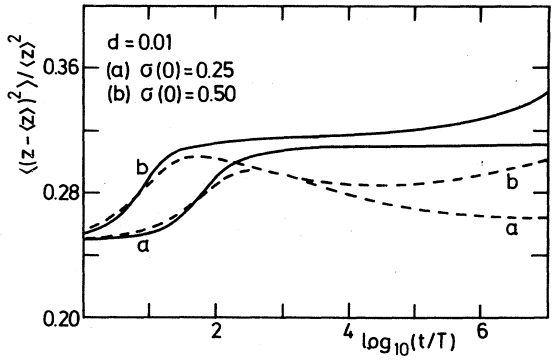

FIG. 6. Relative width of the distribution function as a function of time. Same conditions as Fig. 4.

mer concentration. Therefore, $\dot{q}_2$ is negative and subsystem a gains matter at the expense of subsystem b, compare Fig. 7. In addition, the term proportional to $\dot{\sigma}$ in the equation of motion of $\langle z\rangle$, Eq. (26), implies that $\langle z\rangle_1$ exceeds $\langle z\rangle_2$ (Fig. 5). This in turn has the consequence that x_2 will be bigger than x_1 (Fig. 8) which is explained by a careful inspection of Eq. (27). Both the relative magnitudes of $\langle z\rangle_i$ and x_i tend towards an increased aging rate $\phi(0,t)$, Eqs. (29) and (30), for subsystem b ($i=2$) in comparison with subsystem a ($i=1$). This, finally, explains the observation (Fig. 4) that the particle density $n_2(t)$ decreases more rapidly than $n_1(t)$, compare Eq. (11). The positive-feedback loop which results in the accretion of matter in one subsystem at the expense of the other one essentially stems from the back-reaction of σ on itself through the average particle size $\langle z\rangle$. However, we mention that the symmetric state of an equal distribution of matter between the subsystems is not unconditionally unstable against small fluctuations which break the symmetry. Instead, the coupling constant d has to exceed a certain (time-dependent) threshold. This will be discussed in more detail in Sec. IV.

Finally, we consider a case of even larger diffusional coupling strength, namely $d=0.1$. Figures 8–12 show the results of both theories. We include a graph of the supersaturations $\sigma_i(t)$ (Fig. 9) showing the degree of agreement which is typical for this observable in all the simulations we performed. Dissolution of the particles in subsystem b is rather quick and virtually complete within less than $\tau=10^3$. The simulation of the exact theory was stopped when $q_2(t)$ (curve b in Fig. 12) became indistinguishable from $\sigma_2(t)$ (curve labeled b').

Summarizing, the numerical results of this section have demonstrated that our theory in terms of a few ordinary differential equations represents a fairly accurate approxi-

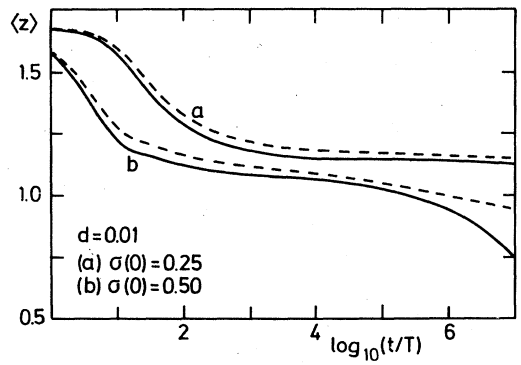

FIG. 5. Mean particle size as a function of time. Same conditions as Fig. 4.

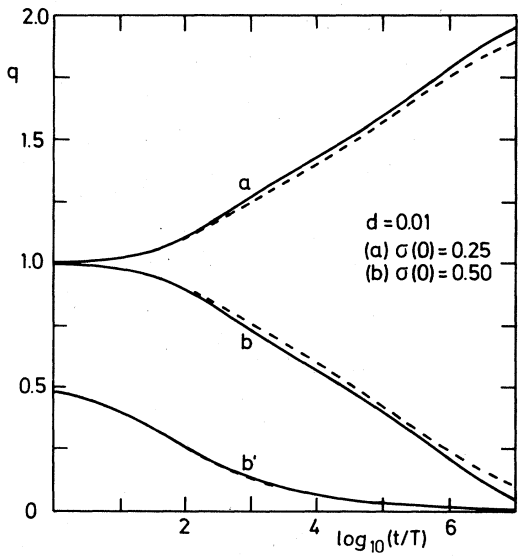

FIG. 7. Total amount of matter in each cell as a function of time. Same conditions as Fig. 4. Curve b' denotes the supersaturation in subsystem b.

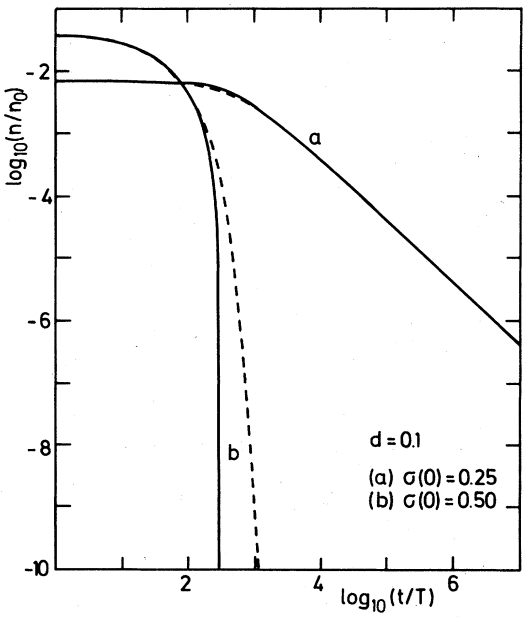

FIG. 8. Particle density for coupled cells ($d=0.1$) with different initial conditions (see inset) as a function of time. Solid lines, approximate theory; dashed lines, exact theory.

mation to the more complete theory for the full size distribution function. The comparison has been performed for closed as well as for coupled open systems with different coupling strengths and extended over 7 orders of magnitude on the reduced time scale $\tau=\lambda t$. In addition, our simulations contain interesting physics if one accepts our idealized model as a prototype for competitive coarsening and growth extending over macroscopic distances.

IV. DISCUSSION

This final section provides suggestions on how our theory may be generalized to go beyond the limit of vanishing volume fraction and how to include the phenomenon of coagulation in an approximate way. Before coming to these points, however, let us consider the effect of competitive coarsening between macroscopic regions (different cells in the model of Sec. III) from a different perspective.

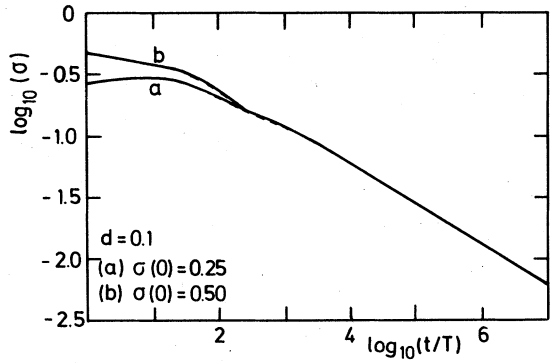

FIG. 9. Supersaturation as a function of time. Same conditions as Fig. 8.

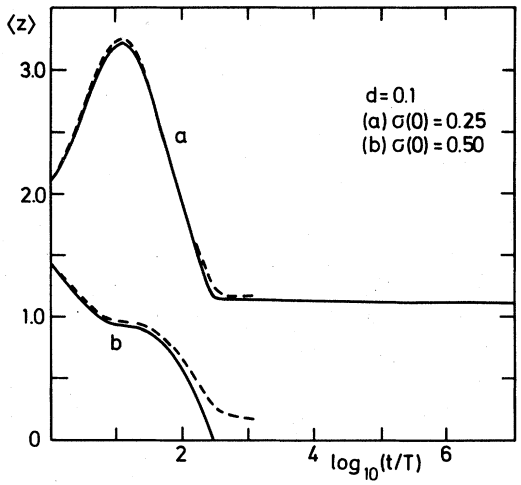

FIG. 10. Mean particle size as a function of time. Same conditions as Fig. 8.

From Eq. (12) which is still exact on the basis of our theoretical starting point, namely Eqs. (1)—(3), one derives the following expression for the time derivative of the mean size $\langle z\rangle$:

$$\langle \dot{z}\rangle = 3\lambda\sigma^3[\langle z^{1/3}-1\rangle+\phi(0,t)\langle z\rangle]+3\frac{\dot{\sigma}}{\sigma}\langle z\rangle \ . \tag{35}$$

If we insert Eq. (15) and use (13) in order to express n in terms of σ, q, and $\langle z\rangle$ we find

$$\langle \dot{z}\rangle = -9\lambda q\sigma^2\left[\left[1-\frac{4\sigma}{3q}\right]\langle z^{1/3}-1\rangle-\frac{\sigma}{3q}\phi(0,t)\langle z\rangle - \frac{\dot{q}}{3\lambda q\sigma^3}\langle z\rangle\right] . \tag{36}$$

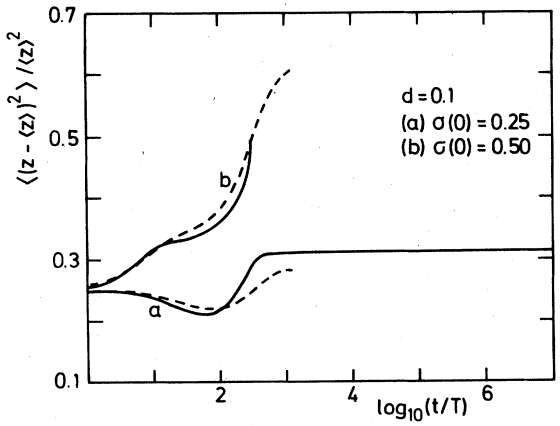

FIG. 11. Relative width of the distribution function as a function of time. Same conditions as Fig. 8.

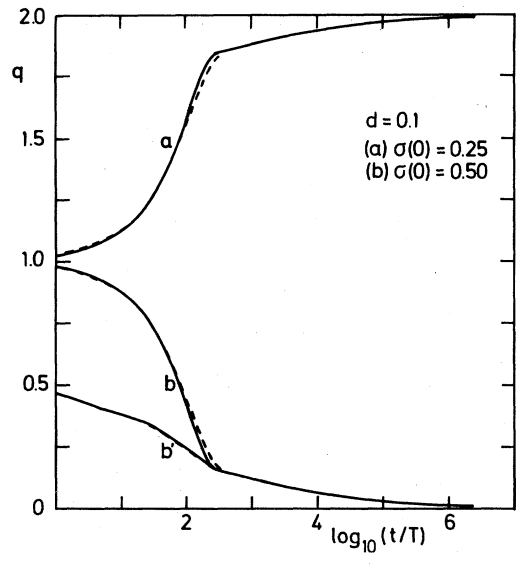

FIG. 12. Total amounts of matter in each cell as a function of time. Same conditions as Fig. 8. Curve b' denotes the supersaturation in subsystem b.

For closed systems with $\bar{q}=0$ and in the limit $\sigma=q$ this reduces to (18). An inspection of (36) indicates that the dynamics of $\langle z\rangle$ will generally be determined by a fixed point which is time dependent but attractive if $\sigma \ll q$ holds and $\dot{q}$ is not too large. The fixed point is determined by

$$\langle z\rangle^{-1}\langle z^{1/3}-1\rangle=\left[1-\frac{4\sigma}{3q}\right]^{-1}\left[\frac{\sigma}{3q}\phi(0,t)+\frac{\dot{q}}{3\lambda q\sigma^3}\right] . \tag{37}$$

We use this equation in order to adiabatically eliminate the expectation values of powers of z from the differential equation for the supersaturation σ. Also, using Eq. (13) again we obtain

$$\left[1-\frac{4\sigma}{3q}\right]\dot{\sigma}\approx-\frac{\sigma}{3q}\dot{q}-\lambda\phi(0,t)\sigma^4\left[1-\frac{\sigma}{q}\right] . \tag{38}$$

The approximate equality stems solely from the adiabatic elimination. Keeping only the lowest-order terms in σ/q and approximating $\phi(0,t)$ by its asymptotic value $\phi(0,\infty)=\frac{4}{27}$ for closed systems we finally have

$$\dot{\sigma}\approx-\frac{\sigma}{3q}\dot{q}-\frac{4}{27}\lambda\sigma^4 . \tag{39}$$

This is of course equivalent to Eq. (20) which holds for closed systems. For open systems we have found the important fact that an increase of the total amount of matter ($\dot{q}>0$) results in an additional decrease of the supersaturation. This is true even if the matter is supplied to the system in the form of monomer flux across the boundary and is the reason for the observed unstable evolution of the model of Sec. III in response to unsymmetrical perturbations.

We conclude our remarks on competition between open systems with a linear stability analysis of the two-cell model. Consider deviations $\delta\sigma$ and δq from the symmetric state $\sigma_i=\bar{\sigma}$ and $q_i=\bar{q}$ ($i=1,2$). In linear approximation we find from Eqs. (32) and (39)

$$\begin{aligned}\delta\dot{\sigma}&\approx\left[\tfrac{2}{3}\lambda d\frac{\bar{\sigma}}{\bar{q}}-\tfrac{16}{27}\lambda\bar{\sigma}^3\right]\delta\sigma ,\\ \delta\dot{q}&=-\lambda d\,\delta\sigma .\end{aligned} \tag{40}$$

The symmetric parts of $\bar{\sigma}$ of the supersaturation and $\bar{q}$ of the total amount of matter fulfill Eq. (20) and $\dot{\bar{q}}=0$, respectively. Equation (40) implies *stable* behavior if

$$d<d_c=\tfrac{8}{9}\bar{q}\bar{\sigma}^2 . \tag{41}$$

The coupling between $\delta\sigma$ and δq is trivial in the sense that the relaxation matrix corresponding to (40) has one vanishing eigenvalue. If one includes corrections in σ/q this eigenvalue becomes negative for sufficiently small d which fulfill (41). We emphasize our conclusion that the coupling strength d has to exceed a (time-dependent) critical value $d_c(t)$ in order to yield unstable evolution within a linear analysis. This is important for the discussion of instability in continuously extended macroscopic systems. There, λd has to be replaced by Dk^2 where D is the monomer diffusion constant and k the wave number of the perturbations. This will be discussed in a separate publication.[17]

Our second remark concerns an approximate extension of our theory beyond the limit of vanishing volume fraction. We follow Marqusee and Ross[11] who derive the renormalized growth law

$$V(r,\sigma)=\frac{Dvc_{\rm eq}(\infty)}{r}(\sigma-\alpha/r)(1+r\sqrt{4\pi n\langle r\rangle}) \tag{42}$$

which has to replace Eq. (3) in our paper. We propose approximations

$$r(4\pi n\langle r\rangle)^{1/2}\approx\langle r\rangle(4\pi n\langle r\rangle)^{1/2}\approx(4\pi n\langle r^3\rangle)^{1/2} , \tag{43}$$

to the correction term. The first approximation amounts to averaging with the distribution function $f(r,t)$ and the second one to the replacement $\langle r\rangle^3\approx\langle r^3\rangle$. Then our theory can be reformulated to contain effects of finite volume fraction by simply replacing the rate constant λ by the following function of σ and q:

$$\lambda\rightarrow\lambda(1+\gamma\sqrt{q-\sigma}) , \tag{44}$$

where $\gamma=[3vc_{\rm eq}(\infty)]^{1/2}$ is an additional material constant typically of the order of 10^{-2}.[14] We note that $\gamma(q-\sigma)^{1/2}=(3\phi)^{1/2}$ where $\varphi=(4\pi/3)n\langle r^3\rangle$ is the volume fraction of the minority phase. For the asymptotic behavior of the supersaturation our extended theory predicts

$$\begin{aligned}\sigma(t)&\approx[\tfrac{4}{9}\lambda t(1+\sqrt{3\phi_\infty})]^{1/3}\\ &\approx(1-0.577\sqrt{\varphi_\infty})(\tfrac{4}{9}\lambda t)^{-1/3}\end{aligned} \tag{45}$$

which has to be compared to the correction $1-0.815(\varphi_\infty)^{1/2}$ obtained by Marqusee and Ross.[11] They performed a more accurate analysis and took into account

the change of the asymptotic distribution function $\phi(z,\infty)$, an effect which is excluded by our approximations (43). Despite the 30% error in the numerical prefactor, we consider the result to be satisfying because it predicts the correct trend. We finally note that the result of the stability analysis for the two-cell model changes qualitatively if the correction (44) is included. The q dependence of the renormalized λ implies a coupling between $\delta\sigma$ and δq which forces the zero eigenvalue to become positive even if d is very small. This is important for the dynamics of long-wavelength perturbations in extended systems.[17]

We finally propose an approximate way to include coagulation of droplets of the minority phase. A particularly simple model of coagulation is provided by the assumption that the rate of coagulation is independent of the sizes of the two particles which collide and form a new and bigger particle. If we denote the coagulation rate by η we obtain the following contributions to our equations of motion:

$$\dot{n}\,|_{\text{coag}}=-\frac{\eta}{2}n^2\,, \tag{46}$$

$$\langle\dot{z}\rangle\,|_{\text{coag}}=\frac{\eta}{2}n\langle z\rangle\,, \tag{47}$$

$$\dot{x}\,|_{\text{coag}}=\frac{\eta}{2}n(1-x)\,. \tag{48}$$

The influence of coagulation obviously depends on the magnitude of η. For "fast coagulation" where the rate of coagulation is limited by the mobility of the particles due to Brownian motion in an aqueous solution one has $\eta\approx 10^{-11}$ cm^3 s^{-1}. It turns out that in this case the contribution of coagulation to coarsening is comparable to that originating from diffusion-controlled Ostwald ripening alone. However, the asymptotic time dependence induced by Eq. (46), for instance, is the same as before, namely $n(t)\propto t^{-1}$. If particle growth is limited by slow interface kinetics one may have coagulation dominating at early times and driving the average particle size $\langle r^3\rangle$ towards values large compared to the size of the critical particle r_c^3, i.e., $\langle z\rangle\gg 1$. At later times coagulation slows down and the approximate equilibrium between particle sizes and supersaturation is restored and Ostwald ripening dominates.

We believe that the approximate theory of aging presented in this paper is sufficiently flexible to include additional effects operative on the time domain of coarsening during a first-order phase transition. We have indicated this for the effects of finite volume fraction and coagulation. The theory can be reformulated for alternative laws for particle growth. The corresponding equations for first-order interface kinetics as well as results of numerical simulations for macroscopic inhomogeneous systems subject to these kinetics have been reported.[10] An interesting application of the theory may also be the study of the effect of externally imposed temporal variations of the physical parameters. Variations of the temperature have been shown experimentally to increase the effective aging rate.[18]

APPENDIX A

This appendix gives an argument to support the ansatz (29) for $\phi(0,t)$ in the limit of a small relative width x of the distribution function $\phi(z,t)$. Assume that $\phi(z,t)$ be given by

$$\phi(z,t)=\tilde{\phi}\left[\frac{z-z_m}{\Delta z}\right]\Big/\int_0^\infty dz\,\tilde{\phi}\left[\frac{z-z_m}{\Delta z}\right]. \tag{A1}$$

$\tilde{\phi}(y)$ is an essentially time-independent scaling function defined for $-\infty<y<\infty$. It is normalized and has zero mean value and a width of unity. It is a unimodal distribution but not necessarily Gaussian. The time dependence of $\phi(z,t)$ enters through the parameters $z_m(t)$ and $\Delta z(t)$. In the limit $\Delta z/z_m\ll 1$ one easily shows $\langle z\rangle\approx z_m$ and $x\approx(\Delta z/z_m)^2$, and Eq. (A1) becomes

$$\phi(z,t)\approx\tilde{\phi}\left[\frac{z-z_m}{\Delta z}\right]\Big/\Delta z\,. \tag{A2}$$

Therefore the value at $z=0$ is

$$\begin{aligned}\phi(0,t)&\approx\tilde{\phi}(-z_m/\Delta z)/\Delta z\\&\approx\langle z\rangle^{-1}\tilde{\phi}(-1/\sqrt{x})/\sqrt{x}\,.\end{aligned} \tag{A3}$$

We identify $\beta(x)=\tilde{\phi}(-1/\sqrt{x})/\sqrt{x}$. Since $y\tilde{\phi}(-y)$ has to be a decreasing function of y for $y\gg 1$ we finally arrived at Eq. (29) with the desired property of $\beta(x)$.

APPENDIX B

We consider the asymptotic [$t\to\infty$ or $\sigma(t)\ll q$ for closed systems] properties of the stationary point with respect to the variables $\langle z\rangle$ and x. Let us first determine its position in phase space, i.e., $\langle z\rangle_\infty$ and x_∞. Because of (19) and (24) we have

$$(1-x_\infty/9)\langle z\rangle_\infty^{1/3}-1=0\,. \tag{B1}$$

From (27) and (B1) using $\phi(0,\infty)=\frac{4}{27}$ one obtains

$$2x_\infty\langle z\rangle_\infty^{-2/3}-\tfrac{4}{9}(1+x_\infty)=0\,. \tag{B2}$$

Elimination of $\langle z\rangle_\infty$ yields

$$x_\infty^3-18x_\infty^2+63x_\infty-18=0 \tag{B3}$$

which gives three real solutions for x_∞. Only $x_\infty\approx 0.313$, however, is acceptable physically because the other two solutions either yield a negative $\langle z\rangle_\infty$ or correspond to an unstable stationary point (see below). The physical solution for the average size follows from (B1), $\langle z\rangle_\infty\approx 1.112$.

Next we perform the linear stability analysis around the asymptotic stationary point just determined. The elements of the relaxation matrix Λ are

$$\Lambda_{11}=\left.\frac{\partial\langle\dot{z}\rangle}{\partial\langle z\rangle}\right|_\infty\approx-3\lambda q\sigma^2\langle z\rangle_\infty^{-1}\,, \tag{B4}$$

$$\Lambda_{12}=\left.\frac{\partial\langle\dot{z}\rangle}{\partial x}\right|_\infty\approx\lambda q\sigma^2\langle z\rangle_\infty^{1/3}\,, \tag{B5}$$

$$\Lambda_{21}=\left.\frac{\partial \dot{x}}{\partial\langle z\rangle}\right|_{\infty}\approx\frac{\lambda\sigma^3}{\langle z\rangle_{\infty}^2}\left\{2x_{\infty}\left[\frac{4}{3}\left[1-\frac{x_{\infty}}{6}\right]\langle z\rangle_{\infty}^{1/3}-3\right]+\tfrac{4}{9}(1+x_{\infty})\langle z\rangle_{\infty}\right\}, \tag{B6}$$

$$\Lambda_{22}=\left.\frac{\partial \dot{x}}{\partial x}\right|_{\infty}\approx\frac{\lambda\sigma^3}{\langle z\rangle_{\infty}}\left\{2\left[3-2\left[1-\frac{x_{\infty}}{3}\right]\langle z\rangle_{\infty}^{1/3}\right]-\frac{4}{9}\left[1+(1+x_{\infty})\frac{\beta'(x_{\infty})}{\beta(x_{\infty})}\right]\times\langle z\rangle_{\infty}\right\}. \tag{B7}$$

Without any calculation one realizes that the trace of $\underline{\Lambda}$ is negative since $|\Lambda_{11}|\gg\Lambda_{22}$ holds because of $\sigma\ll q$. This implies that both the eigenvalues of $\underline{\Lambda}$ are negative if and only if its determinant is positive. After some tedious but straightforward algebra one obtains

$$\det\underline{\Lambda}\approx-\lambda^2 q\sigma^5\langle z\rangle_{\infty}^{-2}[4.957-1.025p(0.313)^{-p}]\,. \tag{B8}$$

We have used the exponential ansatz (30) and the numerical values of $\langle z\rangle_{\infty}$ and x_{∞} given above. It is easy to verify that $\det\underline{\Lambda}$ is positive if $p>p_{\min}\approx 1.2$. This is just the condition for the stationary point to be stable.

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