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Theory of Ostwald ripening invoking Taylor analyticity and a Le Chatelier stability principle

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As an alternative to a variety of algorithms, and particularly to the much-favoured Lifshitz-Slyozov-Wagner (LSW) mathematical method of regularization of a coarsening precipitate manifold to hydrodynamic continuity controlled locally by quasi-steady state volume diffusion, we have reformulated the asymptotic, terminally discrete time-dependent particle radius distribution function f so as to be consistent with an even Taylor expanded free energy density. This consistency is necessitated by statistical isotropy in a coarse-grained phase space, a condition violated by the LSW continuity condition. Stability is demonstrated through the application of a closely related Le Chatelier Principle which also appeared in the LS formulation. Wagner's equivalent was to assume separability of variables as a scaling postulate. The coefficients in our analytic distribution function and the appropriate order parameter are established through Wagner's quadratic limit as the radius goes to zero and the requirement that the largest particle which terminates the stable distribution must also have the maximal surface velocity. Our smoothed asymptotic particle radius distribution function generates the standard $t^{1/3}$ scaling but is sufficiently different than that of LSW and its generalizations as to be easily distinguishable experimentally. Indeed, the experimental distribution functions are demonstrated to strongly favour the present formulation. Since the explicit volume fraction of particles φ does not enter into our treatment and the statistical mean distance between particles goes as $(1-\varphi)^{1/3}$, the onset of functional violations due to diffusion impingement should only occur as φ exceeds 0.3, again in accord with many experiments.

1. Introduction

Many models have been offered for the isothermal asymptotic coarsening of a multidisperse array of near-spherical precipitates [1–5], including the elegant and broadly recognized 1962 Lifshitz-Slyozov-Wagner (LSW) theory [6, 7], but none of these can be claimed as an accurate predictor of the radius distribution function f. As recently as 1994 a new theory of Küpper and Masbaum based upon an analogy with the Cahn-Hilliard equation for spinodal decomposition [8] has been presented. For two-dimensional computational modelling this exhibits strong disagreement with the LSW distribution and this in the direction often favoured by the experiments.

The familiar Ostwald ripening free boundary process, which is driven by the higher solubility of the smaller particles [1, 6, 7], is thermodynamically related to coarsening of order-disorder [9, 10], grain boundary [11] and spinodal arrays [12]. While grain boundary and precipitate coarsening, and multidisperse order-disorder and spinodal coarsening are distinguished by discrete and diffuse particle boundaries, respectively, the dominant asymptotic process is in all cases dissipation of surface free energy. We note in particular that because of the coarse-grained phase space in the present problem at the asymptote, strong distribution differentiability as incorporated in the LSW continuity equation of hydrodynamic origin [6] is in all cases absolutely denied in the approach to a largest particle distribution terminus.

Our main point, shared with others [5, 13, 14], is that the LSW algorithm based upon a very strong differential continuity relation has failed to sufficiently recognize the symmetry, discrete and fluctuating elements of the process [5, 13–15] and for this reason fails to fully accommodate the experimental record.

In LSW theory following Greenwood [1] the starting point is a *quasi-steady* solution of the Fick diffusion equation (Laplace's equation) for a single spherical particle with boundary condition corrected for capillarity. Such an approximation is valid for low initial supersaturation. In Wagner's version which follows the previously outlined convention a very strong differentiability condition which could be fully appropriate to a *microscopically* disperse system (the continuity equation) is applied to the conjectured distribution function $f(R, t)$ for the *mesoscopically* multidisperse manifold in radius R and $\dot{R}$ and this accommodates though does not prove the validity of separation of variables and statistical self-similarity (SSS). LS also adopted the continuity equation but replaced the separability assumption by a Le Chatelier stability condition arriving at the same distribution function and a $t^{1/3}$ aging relation, thus accommodating SSS and establishing the fluctuation roots of such a moderation principle in kinetics (compare deGroot [16] or Prigogine [17]). In our approach, we combine what we regard as the best features of Wagner and LS (Greenwood's first order capillarity correction and its asymptotic implications and Le Chatelier stability, respectively) but eschew the continuity equation which with Kahlweit and Mullins [18, 13] we regard as too strong for a Brownian-like, fluctuating system. We replace this constraint by an explicit Landau symmetry for a statistically isotropic mesoscopic system implying a temporally asymptotic free energy density in R-space as an *even* Taylor expansion in an order parameter proportional to the particle surface area, or R^2, together with the stability requirement that the largest and most probably the fastest growing particle terminate the distribution function. Were this intersection not the most probable or average case there is the potential for long range, low frequency oscillations which denies stability and the assumed isotropy *or* a contradiction in which flux is locally directed from the lower to higher chemical potential. As in LS, asymptotic SSS then proves to be a derived characteristic. This procedure and outcome offers an elementary quantitative pedagogy of the class familiar in the coarsening theories of order-disorder, spinodal decomposition and grain growth.

2. The useable parts of the LSW structure

Wagner [7] following Greenwood [1] offered a transparent development of the interface velocity relation starting with a typical ripening sphere in a dilute array with the local Laplacian or quasi-steady approximation of the diffusion field in the first instance taken as independent of the far field concentration, the latter being introduced indirectly through the first-order effect of capillarity on the interface velocity, viz.,

$$\dot{R} = \frac{\mathrm{d}R}{\mathrm{d}t} = \frac{2\beta D}{R_\mathrm{c} R}\left(1 - \frac{R_\mathrm{c}}{R}\right) \tag{1}$$

where D/R is the characteristic volume diffusion interface velocity which is augmented by supersaturation and decremented by capillarity. Note for subsequent reference, the identity of this form to the steady state, capillarity-limited front velocity of lamellar eutectoids [19]. $\dot{R}$ can be positive or negative depending as to whether R is greater than or less than an average value of critical R_c as determined by the effective time-dependent far field supersaturation. The Greenwood [1] value of

$$\beta = \frac{\sigma C_\mathrm{o} V_\mathrm{m}^2}{N_\mathrm{A} kT} \tag{2}$$

was also adopted by Wagner [7] where σ is the surface tension, C_o is the solubility of a pure precipitate in mol/unit volume and V_m is the molar volume.

In this version of the problem as forced to the continuum, the alloy composition remains implicit within initial R_c or the fixed asymptotic volume fraction which can be arbitrarily chosen in accord with the dilute concentration range of the phase diagram. Since we are only concerned here with long time behaviour, this informational shortfall is of no interest. The surface tension σ as an effective quantity may contain significant contributions from solution free energy, gradient and strain energy, and D may contain contributions from gradient and strain energy. In our model for the distribution function all such thermodynamic contributions are combined within a Landau-type Taylor expansion for the free energy density in R-space. As in LSW, this structure can be corrected for solid state precipitates which are line compounds [7, 20, 21]. By convention, insisting upon sufficient volumetric diluteness of the actual array and therefore of a weak but non-zero initial supersaturation, one takes a sample unit volume sufficiently large that it retains a very large number of particles throughout an experimental time in the hopes that suitable array averages can be defined for R, $\dot{R}$ and R_c, the last average quantity implicitly serving the function of a Langevin fluctuation term as in multidisperse processes such as spinodal decomposition [22, 23].

Proceeding phenomenologically, LSW included the approximate asymptotic volume fraction invariance, and as noted invoked the hydrodynamic continuity constraint which we regard as too strong for a fluctuating mesoscopic process (compare Mullins [13, 14] and Refs. 2, 5 and 8). In general, each nucleated particle designated by R in a more-or-less random array has a distinct environment which need not submit to a uniform matrix composition with a well-defined R_c. Indeed, while this environment necessarily shows a continuous decrease in the very small average supersaturation it will have to sustain substantive upward locally pulsed concentration perturbations due to the roughly half of the particles which are dissolving, and because of the inhomogeneity a low amplitude Brownian random walk and/or surface waves must accrue.

3. An analytic thermodynamic extension of Wagner's volume diffusion theory

We will now demonstrate that there is an alternative way of developing the distribution function $f(R, t)$ per unit of volume per unit of R within Ginzburg-Landau theory based upon a Taylor expansion of the free energy density [9, 24] where $\bar{R}$ is an average radius consistent with but not necessarily equal to R_c as in LSW. Reference to Fig. 1 will now be found helpful in proving that for $R \to 0$, the distribution function f varies as R^2. We know *a priori* that f must vanish for some largest R since the maximum total fractional volume of all particles is some number $\ll 1$. After Wagner, we also know that the average number of particles per unit volume is

$$z = \int_0^\infty f(R, t)\,\mathrm{d}R \tag{3}$$

and the average loss of z in time is given by the number of particles per unit volume which converges to $R = 0$

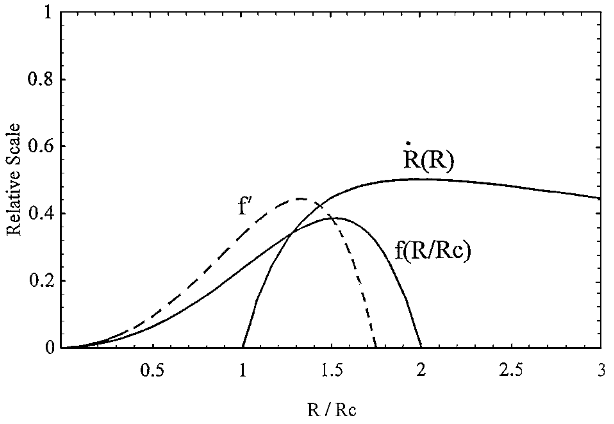

Figure 1 Schematic of $f(R/R_c)$ and $\dot{R}(R)$, the latter according to Wagner [7]. The normalized perturbation of f to f' is designated by the dashed line.

per unit time, i.e., via the limit value of $(-f\dot{R})$ at $R = 0$, viz.,

$$
\begin{aligned}
-\frac{\mathrm{d}z}{\mathrm{d}t} &= -\frac{\mathrm{d}}{\mathrm{d}t}\int_0^\infty f(R,t)\,\mathrm{d}R \\
&= -\int_0^{\mathrm{f}} \dot{R}\,\mathrm{d}f = -\lim_{R\to 0}(f\dot{R}) \qquad (4)
\end{aligned}
$$

In the limit of $R \ll R_c$ from Equation 1 on the right

$$\dot{R} = -\frac{2\beta D}{R^2} \qquad (5)$$

It is highly appropriate here that R_c, which is an ill-defined quantity, disappears from the limiting value of Equation 1, whence as $R \to 0$

$$-\frac{\mathrm{d}z}{\mathrm{d}t} = -\lim_{R\to 0}(f\dot{R}) = \lim_{R\to 0}\frac{2\beta D}{R^2}f \qquad (6)$$

Since according to Wagner (assuming differentiability) $\mathrm{d}z/\mathrm{d}t$ must have a finite value at the limit, it follows that $f(R,t)$ increases proportionately as R^2, already represented schematically in Fig. 1. We emphasize that this result is independent of the LSW continuity conjecture. Further to this we propose to invoke Landau symmetry of the total asymptotic free energy density h in R-space as an average defined by the distribution function, which on account of statistical invariance under the exchange of any $\mathbf{r} \to -\mathbf{r}$ requires that it be an analytic even function of an appropriate order parameter ξ truncated for low to moderate supersaturations at the quartic, and furthermore that the single largest particle which defines $f = 0$ must also be the fastest growing. A qualitative construction of f consistent with Wagner's $\dot{R} \to 0$ limit and the maximum possible $\dot{R}$ according to Greenwood is given by the solid f curve in Fig. 1. As we shall see, the plausible choice of order parameter, $\xi = (R/2R_c)^2$, assures $h \sim \xi f$ is an even function near $R = 0$ and dictates that the general form of h be a quartic at the next level of approximation for $R > 0$.

This *structure* is not unique since it can also be accommodated, due to monotonicity between $f(R)$ and $\dot{R}(R)$, for all f cut-offs in the range $R_c \to 2R_c$, e.g., f' in Fig. 1. However, the only one which will assure consistency asymptotic to the constant maximum value of the particle volume (approximately zero supersaturation [13]) is that with the $2R_c$ cut-off as we shall now demonstrate. Proceeding in the fluctuation context, and analogously to Mullins' rephrasing of LSW [14], if we consider any perturbation to normalized f' by uniform contraction along the R axis subject to particle volume and number conservation the response is always to stabilize the higher R configuration. For example, for any lowered cut-off a larger fraction of the array must be disappearing despite a contradictory decreased maximum size and growth rate. On the other hand, an increased cut-off consistently implies a lower fraction disappearing and increased maximum size and growth rate. For $R = 2R_c$ the perturbation to a higher cut-off has certain smaller particles growing to the disadvantage of the largest one which violates the sign of the known chemical potential difference, so this is the stability point. Consistently, this defines the potential corresponding to the dynamical Le Chatelier Principle as the dissipation rate, for which an externally constrained system in *linear* irreversible thermodynamics is minimal [16, 17]. For the present autonomous non-linear system, it is necessarily maximal because maximality in the surface accumulation rate of a very few large particles at constant volume must be accompanied proportionately by the dissipation of the surface area of a much larger number of surface-rich small particles.

The designation of stability at the $2R_c$ maximum of $\dot{R}$ at fixed R_c in Equation 1 defines the quasisteady scaling law, $R = 2R_c$, so upon substitution in (1), we can integrate over $\dot{R}_c$ so as to generate the asymptotic $t^{1/3}$ scaling law, originally estimated in this way by Greenwood [1], viz.,

$$R_c = (3\beta Dt/4)^{1/3} \qquad (7)$$

The coefficient 3/4 is to be compared with the value 8/9 in the LSW equation for R_c so the results are closely equivalent.

As pointed out some time ago [25], in viewing this as a free-boundary problem with the degeneracy subsumed by the unspecified initial condition, the weighted quasi-steady dissipation rate for an array at $R_c(t)$ can be estimated as proportional to $\mathrm{d}(RR_c)/\mathrm{d}t$ which also maximizes at $R = 2R_c$. This result is in accord with the inferences from the *gradient flows* methodology [26, 27] or from a maximum in the path probability [25, 28, 29]. This viewpoint is analogous to that in the free boundary, capillarity-controlled, two-dimensional spacing problem of eutectoids with its experimentally verified maximal dissipation and equivalent Le Chatelier Principle formulations [19, 30, 31], anticipated by the sharing of equation form (1).

4. The relative distribution function, *f*

Repeating the proposed argument for emphasis, the next step in the construction is to note on account of the $R = 2R_c$ cut-off and Wagner's $R = 0$ limit that f must be designated as a function of $\xi = (R/2R_c)^2$, thus to be recognized as the explicit order parameter for the smoothed surface free energy increments. Then on account of the assumed statistical isotropy or symmetry of the manifold we can demand that the asymptotic relative free energy density function h in R-space be an even, lowest order, truncated Taylor expanded quartic, now used to evaluate the general free density h in R-space, including relative $f(\xi)$ as a multiplying factor to the order parameter ξ at constant t, viz.,

$$h \sim f(\xi)(R/2R_c)^2 \tag{8}$$

With the limits already established for f, and the expectation through f that for R incrementally greater than $2R_c$, $h = 0$, the coefficients in the quartic are uniquely established, viz.,

$$h \sim \xi^2 - \xi^4 = \left(\frac{R}{2R_c}\right)^4 - \left(\frac{R}{2R_c}\right)^8 \tag{9}$$

from which we deduce relative, temporally scaled

$$f = \ell(t)\left(\frac{R}{2R_c}\right)^2\left[1 - \left(\frac{R}{2R_c}\right)^4\right] \tag{10}$$

The solid curve in Fig. 1 was calculated via this form. The inaccuracies inherent in the truncation procedure (which are the primary ones in this methodology) are for the most part compensated by forcing h and f to their explicitly designated terminations. An analogous self-correcting procedure is found in the analytic free energy density pertaining to mean field spinodal decomposition with a symmetric miscibility gap. Here the double well density truncated at the quartic can as an approximation be corrected through the fourth order coefficient by forcing the solubility to zero at $T = 0$ K (the Third Law). Note here that ξf_{LSW} through Wagner's theorem (6) is again even as $R \to 0$ but loses this character as $R \to R_c$ and above, thus violating the symmetry of the statistical manifold, the direct evidence lying in the flat tail of f_{LSW} (Fig. 2) which is inconsistent with statistical concepts.

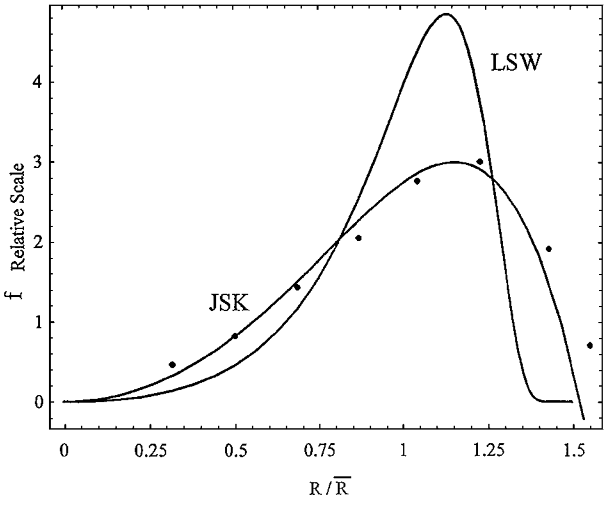

Figure 2 Comparison of present distribution function f with LSW theory and Kahlweit's data set [33] for isoamyl alcohol droplets in water (●).

Note from (9) that it is salutary to the construction that the largest particle ($R = 2R_c$) persists asymptotically in quasi-equilibrium with the highly depleted but non-zero average supersaturation ($h \simeq 0$).

The final step is to evaluate the relative function $\ell(t)$ such that the average particle volume is time invariant [7], viz.,

$$\begin{aligned} V &= \int_0^{2R_c} \frac{4}{3}\pi R^3 f \, \mathrm{d}R \\ &= \int_0^{2R_c} \frac{4}{3}\pi R^3 \ell(t)\left(\frac{R}{2R_c}\right)^2\left[1 - \left(\frac{R}{2R_c}\right)^4\right] \mathrm{d}R \\ &= \text{constant} \end{aligned} \tag{11}$$

from which upon substitution of (7)

$$\ell(t) \sim t^{-4/3} \tag{12}$$

in agreement with Wagner [7] at the asymptote. Furthermore, since

$$\Delta F = \sigma \int_0^{2R_c} 4\pi R^2 f \, \mathrm{d}R \tag{13}$$

our value of f and (12) combined yields

$$\Delta F \sim t^{-1/3} \tag{14}$$

representing a plausible slow relaxation of this broadly-recognized Lyapunov functional [8, 32] in accord with the Second Law on the isotherm. LSW implies the same result.

5. Experimental closure

From the distribution function f in Equation 10, we obtain $\bar{R} = 1.312R_c$ as compared to the LSW $\bar{R} = R_c$. Our cutoff is at $R/\bar{R} = 1.52$ as compared to 1.5 for LSW. The maximum of f is at 1.158 as compared to 1.135 for LSW, the summary comparison being represented in Fig. 2 containing data of Kahlweit [33]. The strange continuum LSW tail in this figure associated with a cancellation of singularities [7] appears to be indicative of a constraint which as applied to a small number of discrete particles is necessarily uninterpretable in relation to experiment.

The revised $\bar{R}$ translates to a rate constant which is 1.1 times that for LSW. It is to be emphasized here that our development does not and could not explicitly depend on the asymptotic volume fraction φ because the composition was not explicitly entered as an initial condition. Since the relative statistical mean distance between particles goes as $(1 - \varphi)^{1/3}$, we estimate via the binomial theorem that diffusion impingement should start to seriously violate the assumptions leading to Equation 1 at $\varphi = 0.3$. There is little experimental evidence in favour of LSW as $\varphi \to 0$ nor of the change in the distribution function and the strong increase in rate constant with φ attributed to theory [34, 35]. Fig. 3 superposes our invariant distribution function on Ardell and Nicholson's data for Al-Ni covering a $\varphi = 0.1$–0.2 range [36]. The agreement for f is everywhere excellent, as was the Fig. 2 case from Kahlweit.

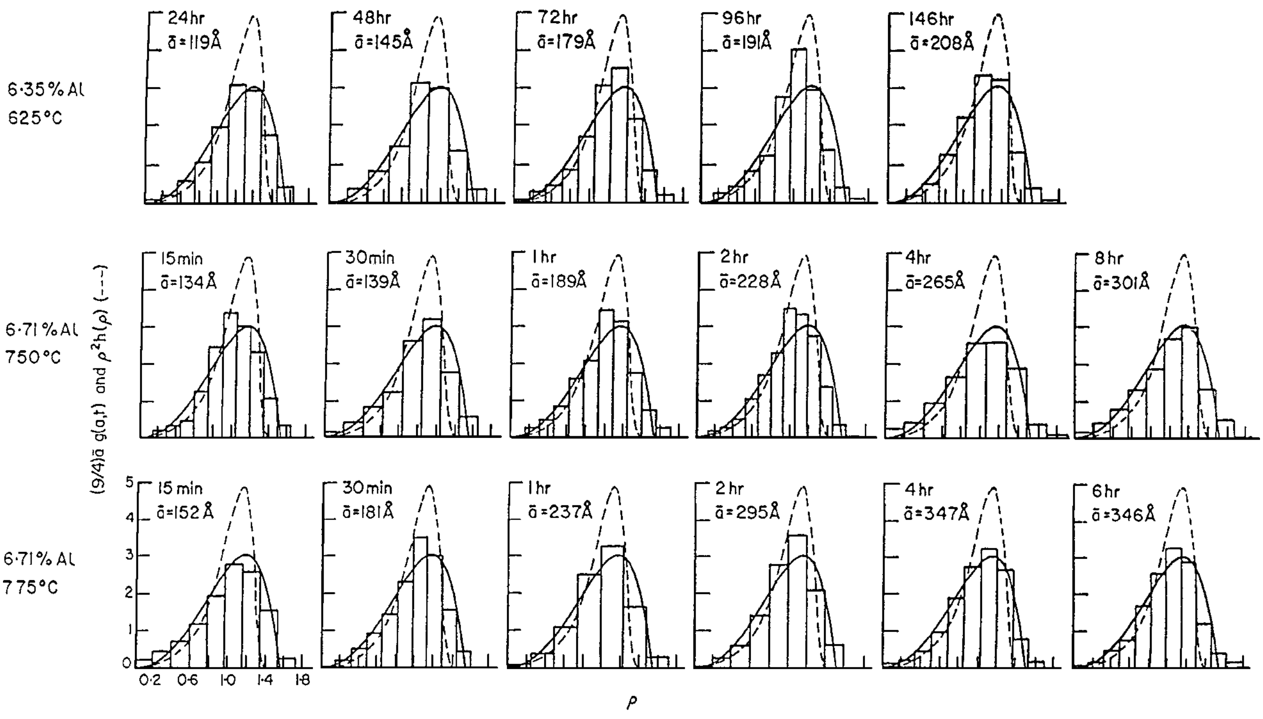

Figure 3 Ardell and Nicholson data set [36] for Ni-Al alloys compared to LSW (- - - -) and present theory (-----). The volume fractions from bottom to top are 0.102 and 0.198, respectively.

While coherency strain is not accounted for, this should enter invariantly through the diffusion coefficient [12] and accordingly only modify the rate constant for $\bar{R}$. The failure to correct D and σ positively as specified above may be the reason why Ardell [35] finds in a survey that the experimental rate constant for $\bar{R}$ scatters over a factor up to 4 times larger than our predicted value. In our quantitative analysis of scaling in cellular solidification, which is related to the eutectoid spacing problem, we found an amplification of the effective surface tension due to near boundary solution free energy by a factor of 6 [25].

6. Discussion

It was Wagner alone who considered the case of interface reaction control [7] which by convention rather unrealistically *specifies* the absence of solute gradients in the matrix. This constraint has the effect of everywhere uniquely equating near and far field concentrations thus eliminating a statistical degree of freedom. As Mullins has clearly implied [13, 14], the LSW use of the continuity equation for the volume diffusion case, makes the problem deterministic rather than accommodating to the fluctuations implied by the actual physics. Here we conclude that for chemical reaction control as in order-disorder the continuity equation may more validly obtain and Wagner's derivation of a $t^{1/2}$ asymptotic scaling law becomes algebraically valid. However, we are not aware of any experimental counterpart to this model.

The distinction between this and the LSW approach to removing the degeneracy associated with an unspecified initial condition hinges mainly upon how strongly the discreteness of the particle distribution is smoothed or regularized. In the LSW case the hydrodynamic continuity equation is forced deterministically by conjecture upon the manifold, and at least for LS theoretical closure is realized through perturbation arguments which is inconsistent if not contradictory. While many investigations have regarded continuity as a rigorous constraint [3, 4, 7, 35, 37] others have properly seen this as an approximation of undetermined precision [2, 5, 8, 18]. From a general view point, it first appeared to us to be an overdetermination, invoking two conservation relations where only one pertaining to the solute in general expressed asymptotically as a constant volume fraction is extant. However, the more cogent defect is that the even statistical symmetry of the free energy density $\xi f(R)$ associated with the smallest particles is not shared by the families of larger particles since ξf_{LSW} is not even. Accordingly, the LSW $h(R)$ and $f(R)$ are statistically defective as $R \to 2R_{\mathrm{c}}$ as evidenced by the experimentally meaningless tail in Fig. 2 and the relatively sharp peak in f. In our case, the *phase* space is assumed to be mesoscopic and statistical, seeking asymptotic, quasi-steady stationarity in a free energy density of *essential* Landau symmetry [38] and this is also represented operationally by the perturbation or Le Chatelier Principle.

It does not appear to have been sufficiently emphasized that for all multidisperse coarsening systems there must exist a late temporal state of few particles where a distribution function loses meaning [8]. We have accordingly meant by an asymptotic state that which has already lost a very large number of particles per test volume in reaching the asymptote but still retains a very large number. Even so, every real system is finite so there must always exist an individual largest particle and this discreteness speaks to the ultimate imperfection of the concept of a continuous distribution function. The problem of discreteness is more acute in the case of Ostwald Ripening as compared to grain growth and multidisperse ordering with their non-conserved order parameters for as a consequence of solute conservation the total particle volume approaches a constant asymptote. The logic then forces us to conclude at the asymptote that if assuming strong continuity and fixed time we theoretically try to reduce the volume fraction or composition incrementally at fixed particle number, particles must be lost, which is a contradiction. In other words, there is no analytic continuation to zero volume fraction, as attribution to LSW theory of a rigorous limit often implies, but experiments deny. This underlines our secondary conclusion: that SSS must within the dilute specification extend in the space of volume fraction as well as along the time axis (cf. Fig. 3).

Considerable effort has been expended in developing supposedly more complete and sophisticated computer algorithms which encompass the pre-asymptotic range of the precipitation process and these are offered a role as generators by curve-fitting for accurate measures of effective surface tensions and diffusion coefficients from structure factor data. The particular version due to Wagner and Kampmann [39] is, however, deterministic and was constructed so as to be asymptotic to LSW so would exhibit the same discrepancies as in Figs 2 and 3 (cf. their Fig. 4–42).

In conclusion, the pedagogic issue addressed here with some success pertains to a method of ascertaining the most quantitative analytic approximation to the properties of a three-dimensional mesoscopic fluctuating phase space with discrete limits and its associated asymptotic domain of self-similar scaling.

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