

Laplace's law and the interfacial momentum source in two-phase models

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A two-phase flow model with liquid-solid transformation [M. Hütter, Phys. Rev. E **64**, 011209 (2001)] is discussed, focusing on two elements: (1) the driving force for nucleation and growth and (2) the contribution of phase interfaces to the momentum balance. According to the model, nucleation and growth are partly driven by deviations from the equilibrium pressure difference between the phases, obtained as the surface tension times the ratio of the rates of change of two structural variables: the interfacial area per unit volume and the solid volume fraction. This is shown to be the proper extension of Laplace's law to nondilute conditions. Contrary to the classical result, the equilibrium pressure difference changes sign at a volume fraction around 50% because the amount of interfacial area lost due to impingement starts to outweigh the amount gained by growth. Hütter did not notice this and consequently misinterpreted a source term in his evolution equation for the momentum density. This term involves the surface tension times the interfacial area per unit volume, which is always nonnegative and hence not related to Laplace's law, as assumed in earlier two-phase models [M. Ishii, *Thermo-Fluid Dynamic Theory of Two-Phase Flow* (Eyrolles, Paris, 1975); J. Ni and C. Beckermann, Metall. Trans. B **22**, 349 (1991)]. An alternative derivation of the interfacial momentum source is presented here, which shows that Hütter's result correctly expresses the balance of forces on a representative volume element and should have been presented as a correction, rather than a corroboration, of the previous works mentioned.

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I. INTRODUCTION

Continuum models for nonisothermal flows of solidifying liquids are necessary, first of all, to gain understanding of the influence of thermal and mechanical loading conditions on the phase change dynamics and, in a later stage, to improve manufacturing processes by means of numerical simulations. A thermodynamically consistent formulation of such a model was derived by Hütter [1], using the “general equation for the nonequilibrium reversible-irreversible coupling” (GENERIC) [2,3]. The Schneider equations, a set of nested differential equations for spherulitic structure development [4], were included in the derivation and extended with convective terms. This should be seen as an important step forward in two-phase flow modeling, since the solid volume fraction and the interfacial area per unit volume, given by the Schneider equations, play important roles in the balance equations for mass, energy, and momentum, as is evident in Hütter's model. Moreover, he obtained an expression for the nucleation rate and the growth rate in terms of the state variables, including the interfacial area per unit volume.

This paper highlights two aspects of Hütter's model. His formulation of the nucleation and growth rates, especially their pressure dependence, is discussed in Sec. III, while the interface-related source term in the momentum balance is analyzed in Sec. IV. The conclusions are summarized in Sec. V. Since the Schneider equations, as formulated in Ref. [1], are of prime importance throughout this paper, these are presented first in Sec. II.

II. SCHNEIDER EQUATIONS

Structure formation is the result of phase change (in the present context, transformation of a continuous liquid into solid spherulites) and convection. These processes are indicated by the subscripts pc and conv, respectively, below. The phase change contributions to structure formation are given by the Schneider equations [4],

$$\dot{\Psi}_0|_{\text{pc}} = \partial_t \Psi_0 - \dot{\Psi}_0|_{\text{conv}} = G \Psi_1, \quad \Psi_0 = V_{\text{tot}}, \quad (1)$$

$$\dot{\Psi}_1|_{\text{pc}} = \partial_t \Psi_1 - \dot{\Psi}_1|_{\text{conv}} = G \Psi_2, \quad \Psi_1 = A_{\text{tot}}, \quad (2)$$

$$\dot{\Psi}_2|_{\text{pc}} = \partial_t \Psi_2 - \dot{\Psi}_2|_{\text{conv}} = G \Psi_3, \quad \Psi_2 = 8 \pi R_{\text{tot}}, \quad (3)$$

$$\dot{\Psi}_3|_{\text{pc}} = \partial_t \Psi_3 - \dot{\Psi}_3|_{\text{conv}} = 8 \pi \alpha, \quad \Psi_3 = 8 \pi N. \quad (4)$$

Here V_{tot} represents the total volume fraction of spherulites, A_{tot} their total surface area per unit volume, R_{tot} the sum of their radii per unit volume, and N their number per unit volume; α and G are the temperature-dependent nucleation rate and radial growth rate, respectively. All these quantities are unrestricted, i.e., nucleation also occurs in the volume already transformed and spherulites interpenetrate without impinging upon each other. Equations (1)–(4) can also be expressed in integral form,

$$\begin{aligned} \Psi_\mu(t) &= \frac{8 \pi}{(3 - \mu)!} \int_{-\infty}^t \alpha(s) \left[\int_s^t G(u) du \right]^{3-\mu} ds \\ &= \frac{8 \pi}{(3 - \mu)!} N(t) \langle R^{3-\mu}(t) \rangle_N \quad (\mu = 0, 1, 2, 3), \end{aligned} \quad (5)$$

with $\langle \dots \rangle_N$ indicating the average over N . Equations (1)–(3) and Eq. (5) for $\mu=0, 1, 2$ can be generalized to describe non-

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spherical growth as well as changes in growth directions [5]. The real volume fraction ϕ can be calculated, for example, by the Kolmogorov-Avrami model [6],

$$\phi = 1 - e^{-\Psi_0}. \quad (6)$$

For a review of Kolmogorov's derivation, see Eder [7,8] or Eder and Janeschitz-Kriegl [9].

Besides the real volume fraction, Hütter's two-phase model contains the real interfacial area per unit volume ψ , which is the part of A_{tot} not overlapped by the solid phase. The real volume fraction obviously increases by outward radial growth from the real interfacial area, hence

$$\psi = \frac{\dot{\phi}|_{pc}}{G} = \frac{d\phi}{d\Psi_0} \Psi_1. \quad (7)$$

Here Eq. (1) has been used. The interface-generating function

$$\mathcal{L} = \frac{\dot{\psi}|_{pc}}{G} = \frac{d\phi}{d\Psi_0} \left(\Psi_2 - \frac{d^2\Psi_0}{d\phi^2} \psi^2 \right) \quad (8)$$

can be derived with the help of Eqs. (1), (2), and (7). Hütter [1] used the variables $\{\phi, \psi, \Psi_2, \Psi_3\}$ to characterize the microstructure. Taking convection into account, he obtained a modified set of Schneider equations, which can be written as

$$D_t \phi \equiv \partial_t \phi + \mathbf{v} \cdot \nabla \phi = G \psi, \quad (9)$$

$$D_t \psi + \frac{1}{3} \psi (\nabla \cdot \mathbf{v}) = G \mathcal{L}, \quad (10)$$

$$D_t \Psi_2 + \frac{2}{3} \Psi_2 (\nabla \cdot \mathbf{v}) = G \Psi_3, \quad (11)$$

$$D_t \Psi_3 + \Psi_3 (\nabla \cdot \mathbf{v}) = 8\pi\alpha. \quad (12)$$

The definition of the material time derivative D_t is given in Eq. (9). The second term on the left-hand side of Eq. (10), (11), or (12) expresses the scaling of the corresponding structural variable under expansion or compression of a volume element.

III. GROWTH RATE AND NUCLEATION RATE

An important outcome of Hütter's model is that the growth rate G and the nucleation rate α obey

$$\frac{G}{\mathcal{R}} = \frac{8\pi\alpha}{\mathcal{R}\mathcal{Q}} = \mathcal{P}(T_s, T_l, T_i, \mu_s, \mu_l) + \frac{1}{T_i} \left(\tilde{p}_s - \tilde{p}_l - \sigma \frac{\mathcal{L}}{\psi} \right), \quad (13)$$

where $\mathcal{R} \geq 0$ and \mathcal{Q} are unspecified functions of the state variables, T_s , T_l , and T_i are the temperatures of the solid (s) phase, the liquid (l) phase, and the interface (i), μ_s and μ_l are the chemical potentials of the phases, \tilde{p}_s and \tilde{p}_l are their intrinsic pressures, and σ is the surface tension. The exact form of the function \mathcal{P} , given in Ref. [1], is omitted here.

The interpretation of the last term in Eq. (13) needs a closer look. In the dilute limit,

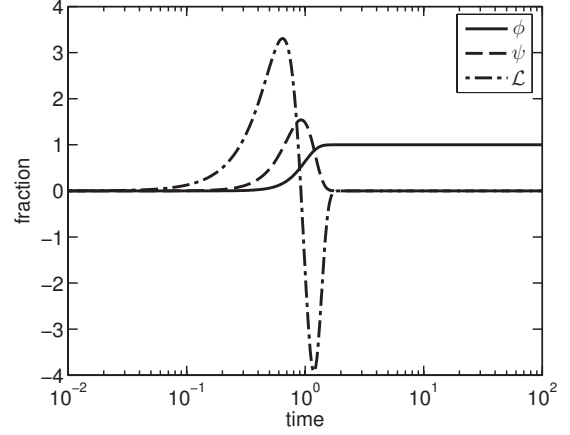


FIG. 1. Volume fraction ϕ , interfacial area per unit volume ψ , and interface-generating function \mathcal{L} for $\alpha=1$ and $G=1$. All units are arbitrary.

$$\lim_{\phi \rightarrow 0} \frac{\mathcal{L}}{\psi} = \frac{\Psi_2}{\Psi_1} = \frac{2\langle R \rangle_N}{\langle R^2 \rangle_N}, \quad (14)$$

which is a measure of the mean curvature of the spherulites. For two phases in equilibrium, Laplace's law relates the pressure difference across the interface to its local curvature H . (In general, $H = R_1^{-1} + R_2^{-1}$, where R_1 and R_2 are the radii of curvature in two orthogonal directions.) Under the assumption that the pressures of the phases in the bulk are equal to their pressures near the interface, it states

$$\tilde{p}_s - \tilde{p}_l = \sigma H. \quad (15)$$

The last term in Eq. (13) suggests that “the beyond-equilibrium situation in terms of a deviation from the recast Laplace equation is a driving force for phase change” (page 9 of Ref. [1]). The word “recast” refers to the appearance of \mathcal{L}/ψ instead of the mean interfacial curvature H . These are equivalent in the dilute limit, as expressed by Eq. (14). However, when spherulites impinge, ψ deviates from Ψ_1 and \mathcal{L} deviates from Ψ_2 . Equation (14) is then violated and the equivalence is lost. The most conspicuous feature of the ratio \mathcal{L}/ψ is that it changes sign. When impingement becomes dominant, further phase change leads to a decrease of ψ and therefore \mathcal{L} becomes negative; see Eq. (8). This is shown to occur at $\phi \approx 0.5$ in Fig. 1. Holding on to the analogy with the classical Laplace equation, i.e., \mathcal{L}/ψ as the mean interfacial curvature, one would conclude that interfaces change from convex to concave, which is unrealistic for solid particles. The key point here is that \mathcal{L} no longer corresponds to a microstructural length scale when spherulites are impinging. Formally, \mathcal{L} is proportional to the sum of radii R_{tot} under dilute conditions only, and that is where Eq. (15) applies.

It is shown below that the modified form of Laplace's law, Eq. (15) with H replaced by \mathcal{L}/ψ , follows from minimization of the free energy with respect to changes in the volume fraction ϕ and the interfacial area ψ . This is implicit in Hütter's approach, because it is based on GENERIC. The surface tension appears as a result of the expression of the total entropy of the system in terms of his chosen state variables, the definition of the interfacial pressure $\tilde{p}_i = -\sigma$, and the require-

ments imposed by GENERIC on the Poisson operator \mathbf{L} for the reversible dynamics. The factor \mathcal{L}/ψ naturally arises from the incorporation of the modified Schneider equations, Eqs. (7), (8), (3), and (4). For details, see Ref. [1].

Modified Laplace equation

Considering a system with constant volume and constant temperature, the equilibrium pressure difference between the phases can be derived by minimizing the Helmholtz free energy $F=E-TS$, where E is the total energy and S is the total entropy of the system. Small variations in F due to small variations in ϕ and ψ are described by

$$\delta F = \frac{\partial F}{\partial \phi} \delta \phi + \frac{\partial F}{\partial \psi} \delta \psi. \quad (16)$$

Here $\delta \phi$ and $\delta \psi$ are due to growth and shrinkage of the spherulites. With Eqs. (7) and (8) one obtains

$$\delta F = \frac{\partial F}{\partial \phi} \psi \delta R + \frac{\partial F}{\partial \psi} \mathcal{L} \delta R, \quad (17)$$

where δR is a small variation in the radius. Using the energy and entropy definitions given in Ref. [1] with $T_s=T_l=T_i$, this can be written as

$$\delta F = -(\bar{p}_s - \bar{p}_l) \psi \delta R + \sigma \mathcal{L} \delta R. \quad (18)$$

The equilibrium condition $\delta F=0$ then yields

$$\bar{p}_s - \bar{p}_l = \sigma \frac{\mathcal{L}}{\psi}, \quad (19)$$

which extends Laplace's law, Eq. (15), to nondilute systems.

For highly curved interfaces, the surface tension is thought to depend on the curvature [10–13]. In the derivation above, this can be taken into account by adding a term to Eq. (16) for variations in the mean interfacial curvature H , which will lead to a corresponding version of Laplace's law. Appendix A offers different possible definitions of H for impinging spherulites. It is shown that, in a phase-transforming system, this requires calculating the evolution of two to four additional structural variables, depending on the definition chosen. It seems worthwhile to repeat the GENERIC analysis of two-phase flow [1] with a curvature-dependent surface tension, to see where and how H enters the balance equations for mass, energy, and momentum as well as the nucleation and growth rates, Eq. (13).

Hütter [14] also derived a more elegant nucleation and growth model, based on the full size distribution of subcritical nuclei, supercritical nuclei, and spherulites. Interestingly, there the ratio \mathcal{L}/ψ did not appear in the phase change equations, except when only the moments of the distribution Ψ_μ were taken into account. In that case a set of differential equations was obtained, which, for a monodisperse distribution, reduces to the Schneider equations. The full distribution model has the disadvantage that it is much less suitable for implementation in numerical simulations. In summary, it is essential to note that the thermodynamically consistent form of the driving force for phase transformation crucially depends on the choice of variables and the level of coarse graining.

IV. MOMENTUM EQUATION

Besides the Schneider equations, extended with convective terms, Hütter [1] obtained a set of evolution equations for the mass and internal energy densities of the phases and the interface, as well as for the momentum density. His results mostly agree with earlier models [15,16], but an important difference is found in the momentum equation, which reads

$$\partial_t \mathbf{u} + \nabla \cdot (\mathbf{v} \mathbf{u}) = -\nabla(p_s + p_l) + \nabla \cdot (\boldsymbol{\tau}_s + \boldsymbol{\tau}_l) + \mathbf{u}^\sigma. \quad (20)$$

Here \mathbf{u} is the momentum density, \mathbf{v} is the velocity, $p_s = \phi \bar{p}_s$ and $p_l = (1-\phi) \bar{p}_l$ are the apparent pressures of the phases, $\boldsymbol{\tau}_s$ and $\boldsymbol{\tau}_l$ are their contributions to the viscous stress tensor, and \mathbf{u}^σ is the interfacial momentum source. According to Ishii [15], the latter equals the gradient of the pressure contribution due to the surface tension,

$$\mathbf{u}^\sigma = \nabla(\phi \sigma H), \quad (21)$$

in which he used Laplace's law, Eq. (15). Ni and Beckermann [16] postulated $\mathbf{u}^\sigma = \sigma H \nabla \phi$, which is equivalent to Ishii's model under the assumption that σ and H are homogeneous. On the other hand, Hütter [1] obtained

$$\mathbf{u}^\sigma = \frac{2}{3} \nabla(\psi \sigma) \quad (22)$$

as a direct consequence of specifying the convection of the structural variables in flow; see Eqs. (9)–(12).

Equations (21) and (22) are equivalent if $H = \frac{2}{3} \psi / \phi$, which indeed reduces to a measure of the mean curvature in the dilute limit,

$$\lim_{\phi \rightarrow 0} \frac{2\psi}{3\phi} = \frac{2\Psi_1}{3\Psi_0} = \frac{2\langle R^2 \rangle_N}{\langle R^3 \rangle_N}. \quad (23)$$

Hütter [1] therefore argued that both models agree on the interfacial momentum source for spherical particles. However, if this is related to the pressure difference between the phases, as assumed by Ishii [15] and Ni and Beckermann [16], H in Eq. (21) should be replaced by \mathcal{L}/ψ , according to the modified Laplace equation, Eq. (19). For a constant nucleation rate α and a constant growth rate G , the result of Eq. (23) is 4/3 times higher than the limiting value of \mathcal{L}/ψ , given by Eq. (14). (Compare H_0 and H_1 at early times in Fig. 3 in Appendix A) More important is the qualitative difference that ψ/ϕ remains positive, whereas \mathcal{L}/ψ becomes negative at $\phi \approx 0.5$, as shown in Fig. 1. This clearly demonstrates that Hütter's result, Eq. (22), is incompatible with earlier works, where the interfacial momentum source was assumed to be related to the pressure difference between the phases.

Derivation of the interfacial momentum source

It is shown here that Eq. (22) is the correct formulation of \mathbf{u}^σ . This could have been anticipated on the basis of two arguments. First, as a result of the antisymmetry requirement on the operator \mathbf{L} , which describes the reversible dynamics in GENERIC, Eq. (22) is accompanied by a term $\frac{2}{3} \psi \sigma (\nabla \cdot \mathbf{v})$ in the interfacial energy balance [1]. This seems physically

correct, since it represents the change of interfacial energy per unit volume due to expansion or compression.

The second argument is based on the physical interpretation of Eqs. (21) and (22). Ishii's formulation, Eq. (21), relates to the pressure difference across the interface, which is already implicitly contained in the pressure term of Eq. (20),

$$p_s + p_l = \phi(\tilde{p}_s - \tilde{p}_l) + \tilde{p}_l = \phi\sigma H + \tilde{p}_l, \quad (24)$$

if Laplace's law, Eq. (15), is applied. The extension to non-dilute systems according to Eq. (19) is irrelevant for the present discussion. Consider the stress-free equilibrium state, in which the momentum density does not change, i.e., the left-hand side of Eq. (20) equals zero, and $\tau_s = \tau_l = \mathbf{0}$. Equation (20) then reduces to

$$\nabla(p_s + p_l) = \mathbf{u}^\sigma. \quad (25)$$

With Eqs. (21) and (24) this yields $\nabla\tilde{p}_l = \mathbf{0}$, irrespective of the gradient of the excess pressure $\phi\sigma H$ due to the surface tension. Intuitively however, if $\phi\sigma H$ varies in space, \tilde{p}_l must vary oppositely to maintain equilibrium.

Hütter's formulation, Eq. (22), relates to the pressure within the interface, i.e., to the surface tension itself, rather than the pressure difference it creates across the interface. Equation (25) then represents a balance between the pressures in the phases and the interface, which is intuitively correct. It is a straightforward exercise to derive this result exactly from the balance of forces on a representative volume element. This derivation is given next, again for the stress-free equilibrium state.

First consider a single spherulite of radius R , which intersects one of the element's surfaces. Due to symmetry, the intersection does not generate a net tangential force on the element. It does generate a net normal force,

$$F_\perp = 2\pi R_a \sigma \sin\theta = \frac{2\pi R_a^2 \sigma}{R}, \quad (26)$$

where R_a is the radius of the intersection and $\theta \in [0, \pi]$ is the angle between the surface and a plane tangential to the spherulite at the intersection. This is illustrated in Fig. 2.

The spherulite could be at any distance $r \in [-R, R]$ from the surface in order to intersect it. If its center of mass lies outside the volume element ($\theta < \pi/2$; Fig. 2) r is positive, if it lies at the surface ($\theta = \pi/2$) $r = 0$, and if it lies inside the element ($\theta > \pi/2$) r is negative. The mean square distance of a large number of similar spherulites is

$$\overline{r^2} = \frac{1}{2R} \int_{-R}^R r^2 dr = \frac{1}{3} R^2 \quad (27)$$

and the mean square radius of their intersections with the surface is

$$\overline{R_a^2} = R^2 - \overline{r^2} = \frac{2}{3} R^2, \quad (28)$$

according to Pythagoras's theorem. From the number density N [see Eq. (4)] the number of intersecting spherulites of radius R per unit area follows as $2RN$. Their mean total normal force per unit area follows from Eqs. (26) and (28).

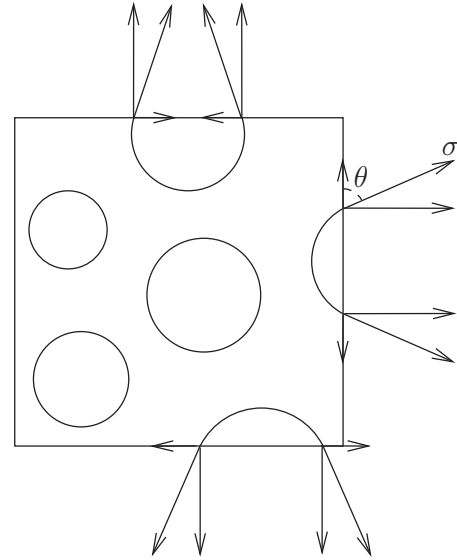


FIG. 2. Tangential and normal forces on the surfaces of a representative volume element due to intersecting interfaces (2D projection shown for simplicity).

Next polydispersity is taken into account. The size distribution $f(R)$ is introduced through

$$N = \int_0^\infty f(R) dR. \quad (29)$$

The number of spherulites intersecting the surface per unit area then becomes

$$N_a = \int_0^\infty 2Rf(R) dR. \quad (30)$$

For any function $X(R)$,

$$N_a \langle X(R) \rangle_{N_a} = \int_0^\infty 2Rf(R)X(R) dR = 2N \langle RX(R) \rangle_N, \quad (31)$$

which, with Eq. (28), can be used to show that the unrestricted area of intersections per unit surface area is equal to Ψ_0 :

$$\Psi_{0a} = \pi N_a \langle \overline{R_a^2} \rangle_{N_a} = \frac{4\pi}{3} N \langle R^3 \rangle_N = \Psi_0. \quad (32)$$

Two important conclusions can be drawn from this result. First, $p_s = \phi\tilde{p}_s$ and $p_l = (1 - \phi)\tilde{p}_l$ are indeed the partial pressures of the phases on a surface.

Second, as explained in Appendix B, the tension due to intersecting interfaces has to be corrected by a factor $d\phi/d\Psi_0$ to account for impingement and to compensate for nucleation in the solid phase. Using Eq. (26), Eqs. (28) and (31), and finally Eqs. (5) and (7), the balance of forces on the volume element yields

$$\begin{aligned}\nabla(p_s + p_l) &= \nabla \left(\frac{d\phi}{d\Psi_0} \int_0^\infty 2Rf(R)\overline{F}_\perp dR \right) \\ &= \frac{2}{3} \nabla \left(\frac{d\phi}{d\Psi_0} 4\pi N \langle R^2 \rangle_N \sigma \right) = \frac{2}{3} \nabla (\psi\sigma),\end{aligned}\quad (33)$$

which confirms Hütter's result, Eq. (22). He obtained this by means of the Hamiltonian mechanics, implicit in GENERIC, which are equivalent to the classical mechanics used in the derivation above. The obvious advantage of GENERIC is that it gives a thermodynamically consistent set of equations, governing both fluid dynamics and phase change of the liquid-solid system. The present treatment focuses on one aspect of the system, the interfacial momentum source \mathbf{u}^σ , supporting our earlier conclusion that it has nothing to do with the pressure difference between the phases. This is obvious because Laplace's law, be it the original Eq. (15) or its extension to nondilute conditions Eq. (19), does not play any role in the derivation of Eq. (22).

V. CONCLUSIONS

Interface-related aspects of Hütter's two-phase flow model including phase transformation [1], based on the non-equilibrium thermodynamics framework GENERIC [2,3], have been analyzed. According to the model, deviations from the equilibrium pressure difference between the phases, given by an extension of Laplace's law to nondilute conditions, act as a driving force for nucleation and growth. A previously unnoticed sign change of this equilibrium pressure difference can be explained in terms of a decrease of the interfacial area per unit volume due to impingement of spherulites. This supports the pressure term of the nucleation and growth rate expressions found in Ref. [1].

An alternative derivation has been given for the interfacial source term in the momentum equation, obtained by Hütter [1]. This term is related to the surface tension, but not to the pressure difference it generates between the phases. Hence it does not involve the mean curvature of the interface, as in earlier two-phase models [15,16], or, according to the modified Laplace equation, the ratio \mathcal{L}/ψ . Trying to make a connection with Refs. [15,16], Hütter interpreted the ratio $2\psi/(3\phi)$ as a measure of the mean interfacial curvature. It has been explained that this interpretation is incorrect in a nondilute solid-liquid system, where the solid particles impinge. Instead of connecting with previous work, it should be stressed that Hütter's model is the first one to give the correct interfacial momentum source. The derivation in this paper is based on a purely mechanical analysis and confirms his result, obtained from GENERIC.

Several opportunities for future work remain. One example is the extension of the model of Hütter *et al.* [5] to nondilute conditions. They derived the analog of the phase change relation Eq. (13) for nonspherical and time-dependent particle shapes, except that they used unrestricted structural variables only. Their result involves Ψ_1 , Ψ_2 , and Ψ_3 . An important question is whether Ψ_3 appears in its role as the number of nuclei or as the rate of change of Ψ_2 . In the

first case, it should be replaced by Ψ'_3 (see Appendix A) whereas, in the second case, it should be replaced by

$$\mathcal{N} = \frac{\dot{\mathcal{L}}|_{pc}}{G} = \frac{d\phi}{d\Psi_0} \left(\Psi_3 - \frac{d^3\Psi_0}{d\phi^3} \psi^3 - 3 \frac{d^2\Psi_0}{d\phi^2} \mathcal{L}\psi \right) \quad (34)$$

analogous to Eq. (8). The answer to this question is unclear from Ref. [5], at least to the present author, and is left as a challenge.

Furthermore, while the surface tension is assumed constant here as well as in Ref. [1], it actually depends on the interfacial strain [12,13,17]. Only in liquid-liquid and liquid-vapor systems, where this strain is canceled by fast migration of molecules from the bulk to the interface, σ remains constant. Curvature dependence of the surface tension can also be incorporated, as explained in Sec. III.

Finally, the two-phase model can be adapted to describe polymer crystallization. It is well known that a polymer spherulite consists of folded-chain crystalline lamellae and amorphous interlamellar domains. Because Hütter's model involves only one surface tension, which acts on the particle-matrix interface, it is not directly applicable to crystallizing polymers. This limitation may be overcome by using two separate surface tensions for the base and lateral interfaces of a lamella with the amorphous phase, respectively, and making appropriate assumptions concerning the total areas of these interfaces per unit volume. The lateral interfacial area may for example be estimated by $\psi_{lat} = \chi\psi$, where χ is the degree of crystallinity.

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APPENDIX A: MEAN INTERFACIAL CURVATURE

When curvature dependence of the surface tension is taken into account, the mean curvature of liquid-solid interfaces H is required. Possible definitions of this quantity are given in this appendix.

A simple geometric argument shows that H should be defined in terms of the *unrestricted* dimensions of the *real* spherulites. The structure after impingement can be imagined as a collection of overlapping spheres. The real interface ψ is the sum of all nonoverlapped surfaces. While ψ decreases upon further growth, the curvatures of the remaining interfaces continue to decrease. On the other hand, the fictitious spherulites nucleated within the volume already transformed (called phantoms by Avrami [6]) do not add to the mean curvature. One can use the modified Schneider equations

$$\dot{\Psi}'_0|_{pc} = G\Psi'_1, \quad (A1)$$

$$\dot{\Psi}'_1|_{pc} = G\Psi'_2, \quad (A2)$$

$$\dot{\Psi}'_2|_{pc} = G\Psi'_3, \quad (A3)$$

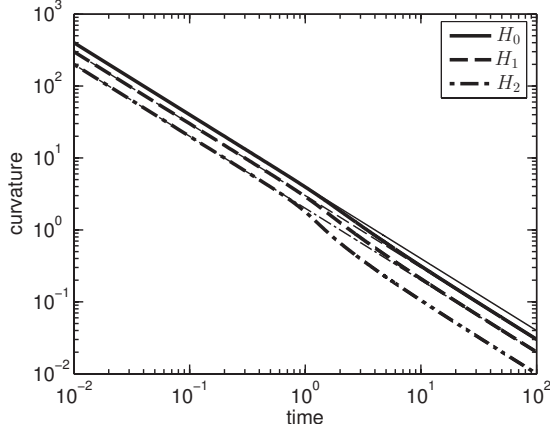


FIG. 3. Mean curvatures H_μ for $\alpha=1$ and $G=1$. All units are arbitrary. Thin lines are mean curvatures including phantoms.

$$\dot{\Psi}'_3|_{\text{pc}} = 8\pi(1-\phi)\alpha, \quad (\text{A4})$$

to calculate the real number of spherulites $N' = \Psi'_3 / (8\pi)$ and their unrestricted dimensions. The integral formulation equivalent to Eqs. (A1)–(A4) is

$$\begin{aligned} \Psi'_\mu(t) &= \frac{8\pi}{(3-\mu)!} \int_{-\infty}^t [1-\phi(s)]\alpha(s) \left[\int_s^t G(u)du \right]^{3-\mu} ds \\ &= \frac{8\pi}{(3-\mu)!} N'(t) \langle R^{3-\mu}(t) \rangle_{N'}, \quad (\mu=0,1,2,3), \end{aligned} \quad (\text{A5})$$

where $\langle \dots \rangle_{N'}$ denotes the average over N' . The mean curvature can be defined in different ways as the ratio of two structural parameters,

$$H_\mu = \frac{2\langle R^{2-\mu} \rangle_{N'}}{\langle R^{3-\mu} \rangle_{N'}} = \frac{2\Psi'_{\mu+1}}{(3-\mu)\Psi'_\mu} \quad (\mu=0,1,2). \quad (\text{A6})$$

Figure 3 shows the differences between the individual H_μ and the effect of excluding the phantoms from the Schneider equations. Phantoms are predominantly created when the volume fraction is large, i.e., at late times, and are therefore on average smaller than the real spherulites. Consequently, each H_μ is smaller than its counterpart with the phantoms included.

APPENDIX B: GROWTH OF INTERSECTIONS

In Eq. (33), the tension due to interfacial forces on the surface of a representative volume element is corrected by a factor $d\phi/d\Psi_0$ to account for impingement and to discard fictitious nuclei, created in the solid phase (phantoms; see Avrami [6] and Appendix A). This correction factor is derived here.

The development of intersections of interfaces with the surface is first described under the assumption of unrestricted nucleation and growth. New intersections appear at a rate

$$\alpha_a = \partial_t \int_0^\infty 2Rf(R)dR = 2GN. \quad (\text{B1})$$

Integrating the right-hand side of Eq. (B1) by parts, we obtain their number per unit area

$$N_a(t) = \int_{-\infty}^t 2\alpha(s) \int_s^t G(u)duds. \quad (\text{B2})$$

Note that this expression and the formulation in terms of the size distribution $f(R)$, Eq. (30), are interchangeable.

According to Eq. (28), the mean square radius of intersections by spherulites of radius R is $\overline{R_a^2} = 2R^2/3$. Therefore the growth rate associated with the area fraction Ψ_{0a} , defined in Eq. (32), equals $\sqrt{2/3}G$. The evolution of Ψ_{0a} is then given by

$$\begin{aligned} \Psi_{0a}(t) &= \pi \int_{-\infty}^t 2\alpha(s) \int_s^t G(u)du \left[\int_s^t \sqrt{\frac{2}{3}}G(u)du \right]^2 ds \\ &= \pi N_a(t) \langle \overline{R_a^2}(t) \rangle_{N_a}, \end{aligned} \quad (\text{B3})$$

which, by comparison to Eq. (5), shows that $\Psi_{0a} = \Psi_0$.

On the other hand, the mean radius of intersections by spherulites of radius R is

$$\overline{R_a} = \frac{1}{2R} \int_{-R}^R \sqrt{R^2 - r^2} dr = \frac{\pi}{4}R. \quad (\text{B4})$$

The mean radial growth rate is thus $\overline{G_a} = \pi G/4$. This also follows from

$$\overline{G_a} = G \overline{\sin \theta} = -\frac{G}{2} \int_\pi^0 \sin^2 \theta d\theta = \frac{\pi}{4}G, \quad (\text{B5})$$

making use of $dr = R d \cos \theta = -R \sin \theta d\theta$ with r and θ being a spherulite's distance and angle relative to the surface; see Sec. IV and Fig. 2. Using $\overline{G_a}$ as the growth rate for all structural variables, successive derivation of Eq. (B3) leads to the following set of differential equations,

$$\dot{\Psi}_{0a}|_{\text{pc}} = \overline{G_a} \Psi_{1a}, \quad \Psi_{0a} = A_{a,tot}, \quad (\text{B6})$$

$$\dot{\Psi}_{1a}|_{\text{pc}} = \overline{G_a} \Psi_{2a}, \quad \Psi_{1a} = \frac{16}{\pi^2} C_{a,tot}, \quad (\text{B7})$$

$$\dot{\Psi}_{2a}|_{\text{pc}} = \frac{64}{\pi} \alpha_a, \quad \Psi_{2a} = \frac{64}{\pi} N_a, \quad (\text{B8})$$

with $A_{a,tot}$ the unrestricted total area fraction and

$$C_{a,tot} = 2\pi N_a \langle \overline{R_a} \rangle_{N_a} \quad (\text{B9})$$

the unrestricted total circumference per unit surface area. The corresponding integral formulation reads

$$\begin{aligned}\Psi_{\mu a}(t) &= \frac{32}{3\pi}(\mu! + 2\mu) \int_{-\infty}^t 2\alpha(s) \\ &\quad \times \int_s^t G(u) du \left[\int_s^t \overline{G_a(u)} du \right]^{2-\mu} ds \\ &= \frac{32}{3\pi}(\mu! + 2\mu) N_a(t) \langle \overline{R_a^{2-\mu}(t)} \rangle_{N_a} \quad (\mu = 0, 1, 2).\end{aligned}\tag{B10}$$

The total tension on the surface due to interfacial forces can be derived from the integral of the mean normal force F_{\perp} over the distribution of intersections,

$$\tau_{\sigma} = c(\phi) \int_0^{\infty} 2Rf(R) \overline{F_{\perp}} dR, \tag{B11}$$

where the factor $c(\phi)$ should compensate for the assumed appearance of nuclei in the solid phase and unrestricted growth of spherulites. Using Eqs. (26) and (B4) in conjunction with

$$\overline{R_a \sin \theta} = \frac{1}{2} \int_{-R}^R \sin^2 \theta dr = \frac{R}{2} \int_{\pi}^0 \sin^2 \theta d \cos \theta = \frac{2}{3} R, \tag{B12}$$

Equation (B11) leads to

$$\begin{aligned}\tau_{\sigma} &= c(\phi) \int_0^{\infty} 2Rf(R) 2\pi R_a \overline{\sin \theta} \sigma dR \\ &= \frac{8}{3\pi} c(\phi) C_{a,tot} \sigma = \frac{\pi}{6} c(\phi) \Psi_{1a} \sigma.\end{aligned}\tag{B13}$$

Thus $c(\phi)$ is identified as a correction of the total circumference of intersections per unit area. Now the real counterparts of Ψ_{0a} and Ψ_{1a} are introduced as ϕ_a and ψ_a , respectively. Since $\Psi_{0a} = \Psi_0$, likewise

$$\phi_a = \phi. \tag{B14}$$

The real total area of intersections increases by outward radial growth from their real total circumference, i.e., the part of $C_{a,tot}$ in contact with the liquid phase. Hence, analogous to Eq. (7),

$$\psi_a = \frac{\dot{\phi}_a|_{pc}}{G_a} = \frac{d\phi_a}{d\Psi_{0a}} \Psi_{1a} = \frac{d\phi}{d\Psi_0} \Psi_{1a}, \tag{B15}$$

where Eq. (B6) has been used. This finally yields

$$c(\phi) = \frac{d\phi}{d\Psi_0} \tag{B16}$$

and Eq. (B13) with $\Psi_{1a} = 4\Psi_1/\pi$ therefore leads to

$$\tau_{\sigma} = \frac{2}{3} \psi \sigma \tag{B17}$$

as seen in Eq. (33).

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- [1] M. Hütter, *Phys. Rev. E* **64**, 011209 (2001).
[2] M. Grmela and H. C. Öttinger, *Phys. Rev. E* **56**, 6620 (1997).
[3] H. C. Öttinger and M. Grmela, *Phys. Rev. E* **56**, 6633 (1997).
[4] W. Schneider, A. Köppl, and J. Berger, *Int. Polym. Process.* **2**, 151 (1988).
[5] M. Hütter, G. C. Rutledge, and R. C. Armstrong, *Phys. Fluids* **17**, 014107 (2005).
[6] M. Avrami, *J. Chem. Phys.* **7**, 1103 (1939); **8**, 212 (1940); **9**, 177 (1941).
[7] G. Eder, in *Macromolecular Design of Polymeric Materials*, edited by K. Hatada, T. Kitayama, and O. Vogl (CRC Press, Boca Raton, FL, 1996).
[8] G. Eder, *Nonlinear Anal. Theory, Methods Appl.* **30**, 3807 (1997).
[9] G. Eder and H. Janeschitz-Kriegl, in *Processing of Polymers*, edited by H. E. H. Meijer (Wiley-VCH, Weinheim, 1997).
[10] R. C. Tolman, *J. Chem. Phys.* **17**, 333 (1949).
[11] V. G. Baidakov, G. Sh. Boltachev, and G. G. Chernykh, *Phys. Rev. E* **70**, 011603 (2004).
[12] A. I. Rusanov, *Surf. Sci. Rep.* **58**, 111 (2005).
[13] F. D. Fischer, T. Waitz, D. Vollath, and N. K. Simha, *Prog. Mater. Sci.* **53**, 481 (2008).
[14] M. Hütter, *Multiscale Model. Simul.* **1**, 371 (2003).
[15] M. Ishii, *Thermo-Fluid Dynamic Theory of Two-Phase Flow* (Eyrolles, Paris, 1975).
[16] J. Ni and C. Beckermann, *Metall. Trans. B* **22**, 349 (1991).
[17] P. Müller and A. Saúl, *Surf. Sci. Rep.* **54**, 157 (2004).