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Phase-Field Simulation of Liquid–Vapor Equilibrium and Evaporation of Fluid Mixtures

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ABSTRACT: In solution processing of thin films, the material layer is deposited from a solution composed of several solutes and solvents. The final morphology and hence the properties of the film often depend on the time needed for the evaporation of the solvents. This is typically the case for organic photoactive or electronic layers. Therefore, it is important to be able to predict the evaporation kinetics of such mixtures. We propose here a new phase-field model for the simulation of evaporating fluid mixtures and simulate their evaporation kinetics. Similar to the Hertz–Knudsen theory, the local liquid–vapor (LV) equilibrium is assumed to be reached at the film surface and evaporation is driven by diffusion away from this gas layer. In the situation where the evaporation is purely driven by the LV equilibrium, the simulations match the behavior expected theoretically from the free energy: for evaporation of pure solvents, the evaporation rate is constant and proportional to the vapor pressure. For mixtures, the evaporation rate is in general strongly time-dependent because of the changing composition of the film. Nevertheless, for highly nonideal mixtures, such as poorly compatible fluids or polymer solutions, the evaporation rate becomes almost constant in the limit of low Biot numbers. The results of the simulation have been successfully compared to experiments on a polystyrene–toluene mixture. The model allows to take into account deformations of the liquid–vapor interface and, therefore, to simulate film roughness or dewetting.

KEYWORDS: film drying, evaporation, phase-field, liquid–vapor equilibrium

INTRODUCTION

Solution deposition of thin films is a widespread and crucial processing route for applications such as membrane technologies, organic electronics,1 third-generation photovoltaics2 including organic or perovskite solar cells,3 batteries,4 and hydrogen-based energy storage and conversion systems.5 In many of these applications, one or more solutes are dissolved in a single solvent or a mixture of solvents, and the film morphology forms during the fabrication process. Depending on the material properties, various desired or undesired processes such as chemical reactions, crystallization, and liquid–liquid phase separation by spinodal decomposition or nucleation and growth can take place. A large part of these transformations occurs during the drying phase because the presence of the solvents allows for fast kinetics. As a consequence, the drying phase is crucial for the film morphology and hence the final film properties and device functionality.6,7

For example, in organic photoactive layers made of an electron donor and an electron acceptor material, it is desired to obtain a so-called “bulk heterojunction” structure, whereby both materials form interpenetrated, well-separated phases at the nanoscale. This ensures good exciton generation within the phases and efficient separation into free charge carriers at the interfaces. Moreover, crystalline phases of both materials should be available to ensure charge extraction.8,9 Such a morphology is crucial to obtain performant devices and has successfully contributed to the improvement of power conversion efficiency to up to 16–18% in the last decade.10,11

It has been therefore recognized that the solvent or solvent blend used for deposition is a tool of choice to gain control over the formation of the morphology.12,13 On the one hand, the thermodynamic properties of the mixture can be modulated in order to trigger or hinder phase transitions. This is typically the case for liquid–liquid phase separation. On the other hand, the evaporation kinetics is determined by the solvents, and the time available for fast structure formation before the film is kinetically “quenched” in the solid state can therefore be adjusted by changing the solvents.

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In order to better understand the process-structure relationship in solution-processed thin films, tremendous efforts have been made to simulate the drying stage of phase separating or crystallizing systems, with various simulation methods from the molecular scale \(^{14,15}\) to the continuum level \(^{16–21}\). Nevertheless, these works focus on the (evaporation-induced) phase transformations in the film, while the description of the evaporation process itself remains rather simple. This may be improved so that the simulated time-dependent concentrations and drying times better match the experimental evidence, which should result in more accurate predictions of the final film morphology.

Significant progress has also been made in continuum simulations of boiling and evaporation with lattice Boltzmann models \(^{22}\) as well as with phase-field or coupled phase-field Navier–Stokes methods. \(^{23–25}\) However, these models do not fulfill all requirements needed in order to use them in simulations of film structure formation, especially simplicity, computational efficiency, and the handling of multicomponent mixtures and of the film surface deformation. Therefore, we recently proposed a simple and efficient phase-field model for the evaporation of fluid mixtures, rendering the evaporation kinetics properly and usable in heavy simulations of evaporation-induced film structure formation. \(^{28}\) However, this model fails at matching all the physics of the evaporation process. In the current work, we propose a still very simple, improved model enabling us to simulate accurately the evaporation rate of pure solvents but also the evaporation kinetics of mixtures.

The basic representation of the evaporation process is given by the so-called Hertz–Knudsen theory. \(^{27,28}\) It is assumed that a gas layer being in thermodynamic equilibrium with the liquid forms directly above the liquid surface. This layer, whose composition is given by the liquid–vapor (LV) equilibrium, contains more solvent molecules than the surrounding environment. Thus, solvent molecules diffuse to the environment, and the evaporation mass flux \(j\) of a pure solvent is given by

\[
j = \sqrt{\frac{M}{2\pi kT}} (\alpha_c P_{\text{sat}} - \alpha_v P_{\text{vap}}) \tag{1}
\]

where \(M\) is the molar mass, \(k\) is the Boltzmann constant, \(T\) is the temperature, \(P_{\text{sat}}\) is the partial pressure in the environment, and \(\alpha_c\) and \(\alpha_v\) are the evaporation and condensation coefficients, respectively. This relationship has turned out to be very successful for the prediction of solvent evaporation rates, despite some inconsistencies with experimental results that led to successive refinements of the theory over the years. \(^{29}\)

In the case of mixtures, the partial pressure of the gas layer close to the film, determined from the LV equilibrium, should be used instead of \(P_{\text{sat}}\) in the equation given above to estimate the evaporation mass flux of each solvent. However, beyond this purely thermodynamic effect, other phenomena might play an important role in the drying kinetics of the blend, especially in the case of polymer solutions. First, the diffusion coefficients are strongly composition-dependent and may drop over several orders of magnitude upon drying, \(^{30–34}\) so that diffusion is too slow to prevent the build-up of concentration gradients close to the surface. This so-called “skin effect” leads to a strong decrease of the evaporation rate at the end of the drying. \(^{26,32,35–37}\) Second, for polymers with a glass-transition temperature higher than the process temperature, the glassy state can be reached in the film when the amount of solvent becomes small upon drying. The drying kinetics is then limited by the relaxation properties of the polymer. \(^{30,38,39}\) Third, in thin polymer films with final thicknesses that are typically in the nanometer range, the final stages of the drying kinetics can be strongly impacted by the reduced mobility of the polymer close to the substrate. \(^{39}\) Fourth, the gas flow in the vapor phase strongly influences the evaporation rate, which is in practice routinely used to vary the drying kinetics with variable air flow rates. \(^{37,40}\) Numerous successful 1D simulations of drying and interdiffusion or sorption experiments, taking these effects into account, have been reported for various multicomponent systems. \(^{32,36–39,41}\)

The objective of the phase-field framework presented in the current paper is to simulate the physical situation described by the Hertz–Knudsen theory. Thereby, the LV interface is not just a boundary condition at the top of the simulation box; it is fully included and can move inside the simulated domain, which contains not only the liquid film but also a gas phase (see Figure 1). In 2D or 3D, with a simple fixed regular mesh, this choice allows for simulations of film structuring upon drying that takes into account possible deformations of the surface and hence predicts, for example, the surface roughness of the dry layer or dewetting phenomena. The present paper is about the validation of the approach and is focused on checking that the behavior which can be expected from the thermodynamics of the drying film is properly recovered. In order to do this, we deliberately ignore all other contributions that might impact the drying kinetics in real systems (diffusion-limited drying, polymer relaxation or confinement, gas flow effects, etc.), except for the comparison with experimental results presented at the end of the paper.

After this introduction, the model is presented in the second section. In the third section, it is compared to the results that can be expected from the theory, for pure solvents first and then for mixtures. A comparison with experiments on a drying
polystyrene (PS)–toluene mixture is also presented, as well as one showcase in 2D considering drying with LV interface deformation. This illustrates the potential of the framework for situations where the surface roughness of the final film or the coverage of the substrate is crucial.

## MODEL EQUATIONS

### Free Energy Functional

The system to be investigated is composed of $n$ fluids that can have a liquid and a vapor phase. Its state is described by the respective volume fractions of these materials $\phi_i$, as well as by an order parameter $\phi_{\text{vap}}$, which varies from 0 in the liquid phase to 1 in the vapor phase. Inspired by classical phase-field methods, we propose a modified version of the free energy already used in our previous model. The total free energy of the system reads

$$G_{\text{tot}} = \int_V (\Delta G_{\text{loc}}^V + \Delta G_{\text{nonloc}}^V) dV$$

where $V$ is the system volume, $\Delta G_{\text{loc}}^V$ is the local free energy density, and $\Delta G_{\text{nonloc}}^V$ is the nonlocal contribution due to the field gradients. The local part of the free energy is given by

$$\Delta G_{\text{loc}}^V(\{\phi_i\}, \phi_{\text{vap}}) = (1 - p(\phi_{\text{vap}})) \Delta G^B(\{\phi_i\}) + p(\phi_{\text{vap}}) \Delta G^v(\{\phi_i\}) + \Delta G_{\text{num}}^V(\{\phi_i\})$$

(3)

The first term on the right-hand side of the equation given above represents the free energy density change upon mixing in the liquid phase for which we use the classical Flory–Huggins theory

$$\Delta G^B(\{\phi_i\}) = \frac{RT}{v_0} \sum_{i=1}^n \frac{\phi_i \ln \phi_i}{\tilde{N}_i} + \sum_{i=1}^n \sum_{j>i} \phi_i \phi_j \chi_{ij}$$

(4)

where $R$ is the gas constant, $T$ is the temperature, $v_0$ is the molar volume of the lattice site considered to calculate the free energy of mixing in the sense of the Flory–Huggins theory, $\tilde{N}_i$ is the molar size of the fluid $i$ in terms of units of the lattice site volume, so that its molar volume is $v_i = \tilde{N}_i v_0$, and $\chi_{ij}$ is the interaction parameter between the amorphous phases of materials $i$ and $j$. In the gas phase, for simplicity, the mixture is assumed to be ideal with gases of the same molecular size, and the local free energy contribution reads

$$\Delta G^v(\{\phi_i\}) = \frac{RT}{v_0} \sum_{i=1}^n \phi_i \ln \left( \frac{P_i}{P_{\text{Sat},i}} \right) = \frac{RT}{v_0} \sum_{i=1}^n \phi_i \ln \left( \frac{\phi_i}{\phi_{\text{Sat},i}} \right)$$

(5)

where we define in the gas phase $\phi_{\text{Sat},i} = P_{\text{Sat},i}/P_0$ and $\phi_i = P_i/P_0$, $P_{\text{Sat},i}$ and $P_i$ are the vapor pressure of the fluid $i$ and its partial pressure in the gas phase, respectively. $P_0$ is a reference pressure that we choose in this work to be the atmospheric pressure without loss of generality. $p(\phi_{\text{vap}})$ is a smooth interpolation function commonly used in phase-field simulations, which ensures the transition from the liquid phase to the vapor phase

$$p(\phi_{\text{vap}}) = \phi_{\text{vap}}^2 (3 - 2\phi_{\text{vap}})$$

(6)

The last term of the free energy functional is a purely numerical contribution to ensure numerical stability that helps maintain the volume fractions between 0 and 1, even for highly incompatible systems or polymer systems where the equilibrium composition of separated phases might be very close to these boundary values

$$\Delta G_{\text{num}}^V(\{\phi_i\}) = \sum_{i=1}^n \frac{\beta}{\phi_i}$$

(7)

$\beta$ and $\gamma$ are numerical coefficients. $\beta$ is chosen as small as possible in order to guarantee numerical stability without significantly modifying the physical behavior of the simulations. The nonlocal contribution of the free energy represents the contribution of surface tension, which originates from volume fraction gradients and phase changes

$$\Delta G_{\text{nonloc}}^V(\nabla \phi_i, \nabla \phi_{\text{vap}})$$

(8)

$\kappa_i$ is the surface tension parameter for the concentration gradient of material $i$, and $\nu_{\text{vap}}$ is the surface tension parameter for the gradient of the order parameter representing the LV transition. Note that especially in the case of polymer mixtures, $\kappa_i$ is supposed to include an entropic part that is composition-dependent and that is related to the chain properties and the interaction parameters. However, we use $\kappa_i$ as a free, constant parameters in this work for simplicity. This is a very common simplification in phase field modeling because its impact on the simulation of liquid—liquid phase separation is practically negligible.

### Kinetic Equations

Classically, the chemical potential $\mu_i$ of a fluid $i$ in the mixture can be defined as

$$\mu_i = \mu_{\text{m}}^i + \frac{\partial \Delta G_{\text{loc}}^i}{\partial x_j} - \sum_{j=1}^n \phi_j \frac{\partial \Delta G_{\text{loc}}^j}{\partial x_j}$$

(9)

In this equation, $\mu_{\text{m}}^i$ is the local molar Gibb’s free energy and $x_j$ is the mole fraction of the fluid $j$. We can extend this definition to incorporate a nonlocal surface tension term, using functional derivatives instead of partial derivatives. By transforming the equation in terms of volume fractions and free energy densities and applying this to the free energy density of mixing $\Delta G_V = \Delta G_V^B + \Delta G_V^\text{nonloc}$, a generalized chemical potential $\mu_{\text{gen}}^i$ and a generalized chemical potential density $\mu_{\text{gen}}^j$ can be defined as

$$\mu_{\text{gen}}^i = \mu_{\text{gen}}^j = \left( \Delta G_V + \delta \Delta G_V \sum_{j=1}^n \phi_j \frac{\delta \Delta G_V}{\delta \phi_j} \right)$$

(10)

If the molar volume is supposed to be constant, the thermodynamic driving force for the evolution of the volume fractions is the exchange chemical potential density that reads for all fluids from 1 to $n-1$ as

$$\mu_{\text{gen}}^i - \mu_{\text{gen}}^{i,n} = \delta \Delta G_V \frac{\delta \Delta G_V}{\delta \phi_i} - \delta \Delta G_V \frac{\delta \Delta G_V}{\delta \phi_n}$$

(11)
The kinetic equation describing the evolution is the so-called Cahn–Hilliard equation, proposed by Cahn and Hilliard for binary mixtures\textsuperscript{43,44} and generalized later for multicomponent mixtures\textsuperscript{35,48,49}

\[
\frac{\partial \phi}{\partial t} = \frac{\nu_0}{RT} V \left[ \sum_{i=1}^{n-1} \Lambda_i \nabla \left( \mu_{V,i}^{\text{gen}} - \mu_{\phi,i}^{\text{gen}} \right) \right] \quad i = 1, \ldots, n - 1
\]

(12)

This equation is the general version of the diffusion equation for a multicomponent mixture, with the Onsager mobility coefficients being symmetric, \( \Lambda_i = \Lambda_j \). It can be shown that the classical diffusion equation is recovered from the Cahn–Hilliard equation when some simplifying assumptions are used (see S1 in Supporting Information).

Here, we make a distinction between the mobility coefficients in the liquid phase \( \Lambda_i^{\text{liq}} \) and the ones in the gas phase \( \Lambda_i^{\text{vap}} \), while the total mobility is interpolated between both as

\[
\Lambda_i = \left( 1 - \phi_i^{\text{vap}} \right) \Lambda_i^{\text{liq}} + \phi_i^{\text{vap}} \Lambda_i^{\text{vap}}
\]

(13)

In the liquid phase, the mobility has to depend not only on the diffusion coefficients but also on the local mixture composition in order to ensure the incompressibility constraint and the Gibbs–Duhem relationship. Several theories have been proposed to derive correct expressions for the flux, among which the “slow-mode theory”\textsuperscript{43} and the “fast-mode theory”\textsuperscript{50} are the most successful ones. Their names come from the fact that the mutual diffusion coefficient in a binary system is controlled by the slowest component in the “slow-mode theory,” while it is controlled by the fastest component in the “fast-mode theory.” Because the controversy between both theories is not fully resolved yet despite significant efforts,\textsuperscript{51–55} both have been implemented in the model. The expressions of the mobility coefficients in the liquid phase read for the fast mode as

\[
\begin{align*}
\Lambda_i^{\text{liq}} &= (1 - \phi_i) \omega_i + \phi_i^2 \sum_{k=1, k \neq i}^{n} \omega_k \\
\Lambda_i^{\text{vap}} &= -(1 - \phi_i) \phi_j \omega_j - (1 - \phi_i) \phi_i \omega_j + \phi_i^2 \sum_{k=1, k \neq j}^{n} \omega_k
\end{align*}
\]

(14)

and for the slow mode as

\[
\begin{align*}
\Lambda_i &= \omega_i \left( 1 - \frac{\omega_j}{\sum_{k=1}^{n} \omega_k} \right) \\
\Lambda_i^{\text{vap}} &= -\omega_i \omega_j \sum_{k=1}^{n} \omega_k
\end{align*}
\]

(15)

Here, the coefficients \( \omega_i \) are related to the self-diffusion coefficients \( D_i^{\text{liq}} \) of the material \( i \) through the relationship \( \omega_i = N_i \phi_i D_i^{\text{liq}} \). The self-diffusion coefficients themselves are usually dependent on the mixture composition, \( D_i^{\text{liq}} = D_i^{\text{liq}}(\phi_i) \). However, unless otherwise specified, they are kept constant in this paper for simplicity, and their values are chosen so high so that diffusion is fast enough to prevent the formation of any concentration gradients. In such conditions, the choice of the fast- or slow-mode theory has no impact on the results.

In the gas phase, the composition dependence of the mutual diffusion coefficients and the coupling between fluxes are known to be weak so that we assume the mobility coefficients to be

\[
\begin{align*}
\Lambda_i^{\text{vap}} &= \phi_i D_i^{\text{vap}} \\
\Lambda_i^{\text{vap}} &= 0
\end{align*}
\]

(16)

where \( D_i^{\text{vap}} \) is the Fickian diffusion coefficient of the gas in the air. The multiplication by \( \phi_i \), in the equation above compensates the thermodynamic factor \( \partial \Delta G_i^{\text{vap}} / \partial \phi_i \) in order to recover the classical Fickian diffusion.

The evolution of the order parameter is given by the classical Allen–Cahn equation

\[
\frac{\partial \phi}{\partial t} = -\frac{\nu_0}{RT} M_{\text{vap}} \frac{\delta \Delta G_{\text{vap}}}{\delta \phi}
\]

(17)

where \( M_{\text{vap}} \) is the mobility coefficient for the LV interface and will be called “interfacial mobility” in the following. It is thus not to be confused with the LV interface displacement speed in the simulation, as will be detailed below.

The Cahn–Hilliard and the Allen–Cahn equations together ensure that the system progressively relaxes toward its thermodynamic equilibrium by minimizing its free energy relative to the volume fractions and the order parameter. A major simplification in this approach is that the density and molar volume of each material are constant and homogeneous over the whole simulation box, equal to the value in the liquid phase. This requires four comments. First, the reason for this simplification is that it allows for limited complexity of the equations; for instance, for the calculation of the driving force \( V(\mu_{\phi,i}^{\text{vap}} - \mu_{\phi,j}^{\text{vap}}) \) in the Cahn–Hilliard equations, the use of eqs 9 and 10 leads to the very simple eq 11 because some terms simplify. This equation is not valid anymore in the case of inhomogeneous molar volumes. Second, this simplification is a good first order approximation in the liquid phase although not exactly correct. Note that the impact of molar volume or density variations can be partly taken into account through the expression of the diffusion coefficient, for instance, using the free volume theory.\textsuperscript{56} Third, the density and molar volumes in the gas phase of the simulation are orders of magnitude too high, so that we do not pretend to simulate the mass transport correctly in the gas phase using the phase-field equations. The impact of the mass transport in the gas phase on the evaporation kinetics is rather taken into account through the expression of the evaporation flux at the boundary of the simulation box. Fourth, this simplification implies that the substantial variations from the liquid phase to the gas phase are not taken into account. Below, we propose a simple correction to the evaporation procedure in order to compensate for this simplification and demonstrate that the expected drying kinetics can be recovered despite this extreme simplification.

**Evaporation Procedure and Material Types.** So far, we have considered the evolution of a closed system. To simulate evaporation, we introduce an outflux boundary condition at each node at the top of the simulation box \( z = z_{\text{max}} \) where the fluids are in the vapor state (Figure 1). The expression of the quantity of solvent \( i \) leaving the box \( j = \text{vap} \) will be discussed in
detail in the next section. We define three classes of materials that can be present and which differ through the parameters used to represent them:

- The solvents are defined by their vapor pressure available from experimental data. For simulations of solvent evaporation, they leave the simulation box, thanks to the boundary condition $j_{vap}^{\text{eq}} = 0$. Moreover, in such a phase-field framework, the volume fractions of solutes in the gas phase cannot be zero. To make sure that the overall proportion of solutes present in the gas phase is negligible as compared to the one in the liquid film, solutes are defined as volatile species but with very low vapor pressure.

- For the simulation of solvent evaporation, because the Cahn–Hilliard equation is a conservation equation, the solvent leaving the simulation box has to be replaced by an additional material that we define as the air. No flux is defined at the boundary for the air because the volume fraction of air is obtained from the conservation of volume, $\sum \phi_i = 1$. The air is supposed to stay in the gas phase, but a residual quantity of air has to be present in the liquid film. To minimize this effect, and although air at room temperature is far beyond the critical point, we define the air as a material with very high vapor pressure compared to all other materials. The Flory–Huggins interaction parameters of the air with all other materials in the liquid phase are then set to zero, but the air contributes to the ideal free energy of mixing according to eq 4.

Finally, and most importantly, the simulation is expected to match the Hertz–Knudsen theory. It has already been emphasized that evaporation is a two-step process. First, a phase transformation occurs generating a gas layer in quasi-static equilibrium with the liquid film. This is represented in the simulation by the order parameter transition from 0 to 1 determined by the Allen–Cahn equation. Second, gas molecules diffuse away from this layer, which is represented by the outflux in the simulation. The fact that the evaporation rate is only related to the diffusion step suggests that it is the limiting one; in other words, that the phase transition step is very fast compared to diffusion away from the Knudsen layer. This is accounted for in the simulation by choosing very high interfacial mobility $M_{\text{vap}}$ in the Allen–Cahn eq 17 so that the LV interface reacts very quickly to any composition change due to the outflux and restores the quasi-static equilibrium.

**Expression of the Evaporation Flux.** Rewriting the Hertz–Knudsen relationship for each solvent $i$ as a volume flux using $M_i = \rho_i N_i \alpha_i$, and assuming that the evaporation and condensation coefficients are equal and have the same value for all solvents, $\alpha_i = \alpha_i = \alpha$, we get the following expression

$$j_{i,\text{HK}} = \alpha \frac{V_0}{2 \pi R T \rho_i} \rho_i (\phi_i^{\text{vap}} - \phi_i^{\infty})$$

(18)

In this equation, $\phi_i^{\text{vap}}$ is defined as $\phi_i^{\text{vap}} = P_i^{\text{vap}} / P_0$ with $P_0$ being the partial pressure in the environment. $\phi_i^{\text{vap}}$ is the mean volume fraction of the fluid $i$ in the gas phase. According to the Hertz–Knudsen picture, the volume fraction in the gas phase just on top of the LV interface should be used, but for realistic parameters, the diffusion in the gas phase is very fast, and it turns out that the composition in the vapor is homogeneous so that $\phi_i^{\text{vap}}$ can be evaluated by simply taking the value at the top boundary.

However, due to the strongly simplifying assumptions of constant density and constant molar volume embedded in the Cahn–Hilliard equation, two adjustments have to be made in order to use the expression given by eq 18. The first adjustment is related to the fact that the quasi-static equilibrium calculated by the model at each time step is not the correct one. On the one hand, the expected equilibrium volume fractions in the liquid and vapor phases can be determined from the free energy density. The equilibrium is defined by equality of the chemical potentials in both phases $\mu_{\text{eq}}^{\text{vap}} = \mu_{\text{eq}}^{\text{liq}}$ for each fluid. Using eq 9 and using $\sum \phi_i = 1$ in both phases, we obtain, for instance, for a binary mixture, the known equation

$$\phi_i^{\text{vap}} = \phi_i^{\text{liq}} \exp ((1 - N_i / N_2)(1 - \phi_i^{\text{vap}}) + N_2 (1 - \phi_2^{\text{vap}})^2)$$

(19)

where $\phi_i^{\text{vap}}$ is the equilibrium volume fraction of fluid 1 in the vapor phase and $\phi_i^{\text{liq}}$ in the liquid phase. The expression for $\phi_i^{\text{vap}}$ is the same with permutation of indices 1 and 2. On the other hand, the equilibrium calculated by the model results from the condition $\sum \phi_i = 1$. Using eq 10, this results in equilibrium volume fractions calculated in the simulation, $\phi_i^{\text{eq,simu}}$, that are related to the expected volume fractions $\phi_i^{\text{eq}}$ by

$$\phi_i^{\text{vap}} = \phi_i^{\text{eq,simu}} \frac{\phi_i^{\text{vap}}}{\phi_i^{\text{eq}}}$$

(20)

Below, we illustrate this behavior for a binary system. The theoretically expected results (eq 19 full lines) are compared to the values obtained from simulations of binary, closed systems. The simulations are initialized with a homogeneous volume fraction in the liquid film and an LV interface separating liquid and vapor. We let the system equilibrate and measure the equilibrium volume fraction of both fluids in the gas phase $\phi_i^{\text{eq,simu}}$. The corrected equilibrium volume fractions $\phi_i^{\text{vap}}$ are then calculated using eq 20 (symbols). Figure 2 shows the result of this procedure for various values of the molar volumes $N_i$ and of the interaction parameter between both solvents.

For perfectly miscible solvents of the same size, the liquid mixture is ideal, and we recover the well-known Raoult behavior. However, as soon as the solvents are of different molar sizes, or are not perfectly miscible, the solution is not ideal anymore and the solubility curve deviates from Raoult’s law, generating Henry-like behavior which is more pronounced with increasing molar size difference and/or interaction parameter. This is a direct consequence of the use of the Flory–Huggins theory for the free energy of mixing in the liquid. For solvents with the same molar volume, the solubility curves are identical for both solvents, while they are distinct as soon as the molar volumes become different. Note that for $N_2 = 5$ and $\chi = 1$, the volume fraction of fluid 1 (the smallest component) is already almost constant over a liquid volume fraction ranging from 0.5 to 1. The simulation results are perfectly consistent with the theoretical predictions, which demonstrates that the expected LV equilibrium can be derived from the phase-field simulation although the density and molar volume variations are ignored. As a consequence, by inserting eq 20 in eq 18, we adjust the expression of the outflux as

$$j_{i,\text{HK}} = \alpha \frac{V_0}{2 \pi R T \rho_i} \rho_i (\phi_i^{\text{vap}} - \phi_i^{\infty})$$

(18)
integrating this out. The interface is moving to the left.

Figure 2. Equilibrium volume fraction in the gas phase vs the volume fraction in the liquid phase for fluid 1; comparison of theoretical values (full lines) and values deduced from simulations (symbols).

\[ j_{i,\text{HK}} = \alpha \sqrt{\frac{v_0}{2\pi RT}} \frac{N_i}{\rho_i} \left( \frac{\phi_{i,\text{simu}}^{\text{vap}}}{\phi_{i,\text{sat}}^{\text{vap}}} \right)^N_i - \phi_i^{\infty} \]  

The second adjustment is due to the fact that in our model, the densities are simplified to be constant even upon phase change. As a consequence, the volume of solvent contained in the gas phase is not always negligible compared to the one in the liquid film, as illustrated in Figure 3, which significantly changes the mass balance for the solvent. This has to be compensated for in order to recover the Hertz–Knudsen behavior. Let us define the outflux for the solvent \( i \) at each node of the upper boundary of the simulation box as \( j_{i,z=z_{\text{max}}} \). By integrating this outflux at the upper boundary, the total volume variation \( dV_i \) of the solvent \( i \) in the box is

\[ \frac{dV_i}{dt} = \int_{z=z_{\text{max}}}^{z=0} j_i(z) \, dz \]

(22)

If the volume fraction of solvents in the gas phase would be zero, this mass loss would be entirely converted to a mean displacement of the LV interface with the velocity \( v_{\text{int}} \). Using \( j_{i,z=z_{\text{max}}} = j_{i,\text{HK}} \), we would get

\[ v_{\text{int}} = \sum_{i \in \{\text{sol} \}} \sum_{z=z_{\text{max}}} \lambda_{i,\text{HK}} \]

(23)

which is the desired Hertz–Knudsen evaporation rate for a fluid mixture.

However, with non-negligible quantities of solvent in the gas phase (see Figure 3), the outflux has to generate not only the desired mass loss of the liquid film \( S_{i,\text{HK}} \) (\( S \) being the surface of the simulation box, \( S = \sum_{i \in \{\text{dxy} \}} \)) but also the mass increase \( S_{i,\text{HK}} \phi_{i,\text{simu}}^{\text{vap}} \) of solvent in the gas phase due to the displacement of the interface to the left and the mass loss of the solvent \( S(v_{\text{int}} + \frac{z_{\text{max}} \Gamma_{vap}}{d t}) \Delta \phi_{i,\text{simu}}^{\text{vap}} \) in the gas phase due to its volume fraction variation. Here, \( \Delta \phi_{i,\text{simu}}^{\text{vap}} \) is the volume fraction variation in the vapor phase during one time step, and \( \Gamma_{vap} \) is the proportion of the vapor phase in the whole box and thus \( \frac{z_{\text{max}} \Gamma_{vap}}{d t} \) the mean vapor height in the box. This mass balance leads to the final expression of the outflux implemented at the upper boundary of the simulation box

\[ j_{i,z=z_{\text{max}}} = \lambda_{i,\text{HK}} - (\phi_{i,\text{simu}}^{\text{vap}} + \Delta \phi_{i,\text{simu}}^{\text{vap}}) \sum_{k \in \{\text{sol} \}} \lambda_{k,\text{HK}} \]

(24)

Computational Details. The coupled kinetic eqs 12 to 17 with the boundary conditions (eqs 21 and 24), and using the free energy density defined by eqs 2 to 8 are implemented with a finite volume scheme. They are written in a dimensionless form using \( \Delta G_V = v_{\text{loc}} - \Delta G_V^{\text{loc}} / g_{\text{vap}}, \Delta G_V^{\text{nonloc}} = \Delta G_V^{\text{nonloc}} / g_{\text{vap}} \), \( t = t_{\text{sc}} \), \( \tilde{\lambda} = \tilde{\lambda}_{\text{sc}} = \lambda_{\text{sc}} \), \( \tilde{\lambda} = \lambda_{\text{sc}} \), and \( t_{\text{sc}} \) as chosen so that \( g_{\text{vap}} = RT / v_{\text{int}} t_{\text{sc}} = \frac{\max(\kappa_{l,n}, e_{\text{vap}})}{s_{\text{vap}}} \) to be consistent with the size of the thinnest interface of the system, \( D_{\text{sc}} = \max(N D_{\text{sc}}) \), and finally \( t_{\text{sc}} = t_{\text{sc}} / D_{\text{sc}} \).

The equations are numerically solved simultaneously using an Euler backward implicit scheme with variable time steps, which is the main numerical improvement compared to our previous work.\textsuperscript{26} For this, both Allen–Cahn and Cahn–Hilliard equations are linearized and solved together with a direct solver, the Cahn–Hilliard equation being written in the split form.\textsuperscript{58} This implicit implementation is a crucial prerequisite to perform such simulations with complete decoupling of several different time scales, namely the very fast diffusion processes in the simulated domain (related to the Cahn–Hilliard equation), the still fast build-up of the LV equilibrium at the film surface (related to the Allen–Cahn equation), and the very slow evaporation process (related to the outflux). Indeed, an explicit implementation would suffer from drastic limitations of the time steps in order to ensure

![Figure 3. Snapshot of the total solvent volume fraction at two different times \( t_1 \) (black) and \( t_2 \) (blue) during evaporation. The liquid phase is on the left and the gas phase on the right, and the L–V interface is moving to the left.](image-url)
numerical stability. If using realistic input parameters, this would imply unaffordable computational time, even for small 1D simulations like the ones presented in this work and despite any parallel implementation. Inversely, the Euler backward method is unconditionally stable and allows for the use of much larger time steps.

We use a simple heuristic strategy to adapt the time step. It is of course required that all volume fractions everywhere in the simulation box lie in the \(0,1\) interval (0 and 1 being mathematically excluded, see for instance eq 4). If this condition is fulfilled with the calculated solution, the time step is increased by 20% for the next time increment. Otherwise, the time increment is rejected and recalculated with a twice smaller time step. Moreover, an upper limit is set to the time step with respect to the Courant–Friederichs–Lewy (CFL) criterion calculated using the expected interface velocity (eq 23), \(\Delta t < C_{\text{CFL}}\Delta x/v_{\text{int}}(t)\).

Our code is natively 3D and implemented in parallel, but most of the simulations shown in this work are 1D simulations with a lattice of 512 nodes (pure solvent evaporation and two solvent evaporation) or 2048 lattice nodes (solute deposition) performed on a single CPU core. The lattice resolution is \(\Delta x = 1\) nm, and the CFL criterion is calculated with \(0.03 < C_{\text{CFL}} < 0.3\). Under these conditions, the simulations require a few minutes for 500 to 15 000 time steps. It has been verified that they were converged in time by checking that the results remain unchanged with a significantly more restrictive CFL criterion. The spatial convergence has also been verified on the test cases with the thinnest LV interfaces by using various lattice resolutions. The parameters used in the simulation, unless specified in the text, are summarized in Table 1. \(P_{\text{sat,air}}\)

Table 1. Basic Parameter Set for the Simulations

| Parameter | Value |
|-----------|-------|
| \(T\)     | 300 K |
| \(\rho_i\) (all) | 1000 kg/m³ |
| \(v_0\) | \(3 \times 10^{-5}\) m³/mol |
| \(N_{\text{at}}\) | 1 |
| \(N_i\) (others) | see text |
| \(\varepsilon\) | see text |
| \(P_{\text{sat,air}}\) | \(10^9\) Pa |
| \(P_{\text{sat, solute}}\) | \(10^2\) Pa |
| \(P_{\text{sat, others}}\) | see text |
| \(P_{\text{sat}}\) | \(0\) Pa |
| \(\kappa_i\) (all) | \(6 \times 10^{-10}\) J/m |
| \(\epsilon_{\text{cap}}\) | \(9 \times 10^{-5}\) (J/m)⁰.⁵ |
| \(D_{\text{cap}}\) (all) | \(2 \times 10^{-9}\) m²/s |
| \(D_{\text{cap}}^{\text{eff}}\) (all) | \(10^{-5}\) m²/s |
| \(M_{\text{cap}}\) | \(10^6\) s⁻¹ |
| \(\alpha\) | \(-2.3 \times 10^{-5}\) |
| \(\beta\) | \(10^{-7}\) |
| \(\gamma\) | 1 |

and \(P_{\text{sat, solute}}\) are handled as adjustable parameters that are chosen respectively as high and as low as possible, so that the volume fraction of air in the film and of solute in the gas phase be as low as possible, while ensuring a stable numerical resolution. Likewise, we choose \(\epsilon_{\text{cap}}\) and the \(\kappa_i\) parameters as small as possible in order to obtain a numerically tractable interface thickness with a grid spacing of 1 nm in all simulations presented here (unless specified otherwise). The LV interface profile can be quite sharp with volume fractions coming close to 0 and 1, and the numerical contribution to the free energy (eq 7) helps stabilize the resolution, even with the low value of the coefficient \(\beta\) chosen here.

\section*{RESULTS}

**Evaporation of Pure Solvents.** We first turn to the simulation of the evaporation of a single solvent. The system is composed of the solvent itself plus the air. The typical volume fraction field and order parameter field in such a situation are shown in Figure 4. As expected, the solvent volume fraction in the gas phase is homogeneous, constant, and equal to \(P_{\text{sat}}/P_0\).

We checked that, as expected, the solvent evaporates at a constant evaporation rate until it disappears almost completely from the simulation domain (not shown). This shows that the LV quasi-static equilibrium is reached at any time during the evaporation. Additionally, it has been verified that once the interfacial mobility \(M_{\text{cap}}\) is sufficiently high, the evaporation rate is fully insensitive to the surface tension parameters \(\kappa_i\) and \(\epsilon_{\text{cap}}\) and to \(M_{\text{cap}}\) itself (not shown). This validates our approach and confirms that the quasi-static equilibrium condition is fulfilled and that the evaporation is diffusion limited as depicted in the Hertz–Knudsen theory. This also proves the choice of concentration-independent \(\kappa_i\) coefficients as an acceptable simplification here.

Therefore, we expect the evaporation rate to be exactly given by the Hertz–Knudsen relationship. This is evidenced by the results shown in Figure 5. The product \(P_{\text{sat}}\sqrt{N}\) has been varied over four orders of magnitude, and the simulated evaporation rates almost match the expected values. A deviation is observed for both curves \(N = 1\) and \(N = 5\) when the vapor pressure and hence the volume fraction in the gas phase are very low. This is due to the numerical contribution to the free energy (eq 7), which is not negligible anymore and modifies the equilibrium. For pure solvents, this is not a problem because \(P_0\) can be chosen so that the volume fraction in the gas phase is in a satisfactory range. For simulations of solvent blends, however, this implies that the vapor pressures of all solvents may differ by roughly three decades at most. We believe that this is not restrictive for practical cases.

As a consequence, the evaporation rate from our simulations is perfectly known and given by eq 23, and because the coefficient \(\alpha\) is not allowed to vary with the solvent, we can compare the results to experimentally measured evaporation rates for different solvents. For this, we use the data from ref 59. Thereby, the mass evaporation rates are converted to volume evaporation rates. The partial pressure in the environment is assumed to be negligible. The results are shown in Figure 6, relative to the evaporation rate of toluene. This is in fact a check of the validity of the Hertz–Knudsen relationship, which shows good agreement with the experimental data with some discrepancies. Our simulations behave identically, and possible differences between simulations and experiments might be due to the fact that we use a very simple version of the Hertz–Knudsen relationship. The refinement of this theory reviewed in ref 29 can be easily accounted for by simply changing the expression of the outflux (eq 18) in the future, but this goes beyond the scope of the current paper.

Finally, we investigate the surface tension dependence of the solvents on their vapor pressure. This is known experimentally to vary smoothly with \(\ln(P_{\text{sat}})\). We calculate the surface tension \(\sigma\) from the simulations at different vapor pressures by the classical van der Waals formula applied to the volume fraction...
and order parameter gradients (all other parameters remain constant)

\[
\sigma = (\kappa_i + \kappa_z) \int \left( \frac{d\phi}{dz} \right)^2 dz + \phi_{vap}^2 \int \left( \frac{d\phi_{vap}}{dz} \right)^2 dz
\]  

Here, the integral is taken over the interface from one phase to the other. The comparison with experimental data taken from\(^5\) and for a selection of solvent used in organic photovoltaics (data from Hansen’s solvent database\(^6\)) is shown in Figure 7. Quantitatively, the simulated surface tensions are more than one order of magnitude higher than the experimental values. This is expected because the surface tension parameters have been adjusted to generate interface thicknesses of at least 5–6 nm that can be resolved with the chosen 1 nm grid spacing. This is a well-known drawback of phase-field simulations, and this is absolutely not a problem here, even for quantitative simulations, because the evaporation rates are fully independent of the LV interface properties. Qualitatively, the simulated surface tension follows the experimental tendency very nicely. Nevertheless, a deviation can be seen at high vapor pressure, which can be explained easily. In this range, the simulated solvent volume fractions in the vapor phase are far from zero, leading to an underestimation of the volume fraction gradients and hence of the surface tension. The simulated surface tension values shown in Figure 7 have been calculated with the same values of \(\kappa_i\) for all solvents, whereas it is expected to be solvent-dependent. This explains the considerable deviations between simulated and experimental values. In principle, these deviations can be suppressed by mapping the \(\kappa_i\) parameters of the solvents to the experimental surface tensions.

**Evaporation of Fluid Mixtures: Solvent Blends.** To investigate the evaporation behavior of fluid mixtures, we first simulate the evaporation of a binary solvent blend without solutes. For the first solvent, the molar volume is set equal to three times the one of the air (\(N = 3\)), and the vapor pressure...
is fixed to the one of toluene at room temperature (20 °C, 2800 Pa, φ_{sat} = 0.028). The liquid film is a 50:50 blend at the beginning of the simulation. We vary the vapor pressure and the molar volume of the second solvent, as well as the interaction parameter between both solvents. Compared to the case of a pure solvent, the evaporation rate is expected to vary with time as soon as the solvents are different or not perfectly miscible.

We first confirm again that the simulation produces a ternary solvent—solvent—air LV quasi-static equilibrium at any time. To do this, we solve the ternary equilibrium expected from the condition \( \mu_{V1}^{\text{liq}} = \mu_{V2}^{\text{vap}} \) numerically (see S2 in Supporting Information) and compare to the volume fractions given by the simulation at each time step. We find perfect agreement (not shown).

We then compare the simulated evaporation rates to the ones that are expected for a binary (without air) solvent—solvent equilibrium. To obtain the theoretical curve, we use the kinetic equation of the interface displacement which is given by

\[
\frac{dh}{dt} = \sum_{i=1}^{2} v_i(t) = \sum_{i=1}^{2} \alpha \sqrt{\frac{v_0}{2\pi RT \mu_i}} \rho_i (\phi_{vap,i}(\phi_{vap,i}^{\text{liq}}) - \phi_{vap,i}^{\infty})
\]  

(26)

where \( h \) is the film height and \( \phi_{vap,i}(\phi_{vap,i}^{\text{liq}}) \) is given by eq 19. In parallel, the evolution of the total volume of both fluids \( V_1 \) and \( V_2 \) is given by

\[
\frac{dV_i}{dt} = S h_i
\]  

(27)

where \( S \) is the film surface. The volume fraction variation of the first fluid in the liquid phase is given by

\[
\phi_{vap,1}^{\text{liq}} = \frac{V_1}{V_1 + V_2}
\]  

(28)

To compare with the simulation results, we numerically integrate eqs 26–28 from the initial conditions used in the simulation. The results of this procedure are shown in Figure 8 for various vapor pressures and molar volumes of the second solvent, as well as different interaction parameters between both solvents.

Except when both solvents are identical and perfectly compatible (black curve), the overall evaporation rate is in general time-dependent. This effect finds its origin in the constantly changing LV equilibrium. With two solvents evaporating at different speeds, the composition of the liquid film is constantly changing. For solvents of the same molar volume (blue curve), the overall evaporation rate, which is determined at the beginning by the fastest evaporating solvent (the one with the highest vapor pressure), slowly decreases to reach the evaporation rate of the slowest solvent when the fastest evaporating solvent has disappeared. For solvents with different molar volumes and identical vapor pressures, the “fastest” evaporating solvent, if it was alone, would be the one with the highest molar volume due to the \( \sqrt{N} \) prefactor in the Hertz–Knudsen formula. However, in the blend, due to the LV equilibrium, the partial pressure of this solvent is substantially lower, as illustrated in Figure 2. As a result, the evaporation rate of this “fastest” evaporating solvent is lower, its volume fraction increases progressively and therefore the overall evaporation rate increases as well (green curve). When both molar volume and vapor pressure of the solvents are distinct, the effect of the vapor pressure can compensate for the effect of the molar volume and the evaporation rate can be either increasing or decreasing.

The simulation results are in very good agreement with the theoretical expectations. This proves again that the Hertz–Knudsen picture of solvent evaporation is reproduced and that the presence of the air in the simulation does not significantly perturb the calculated quasi-static LV equilibrium. For the simulations with \( P_{sat} = 5P_{sat1} \), we recover the theoretical results despite a very significant amount of solvent in the gas phase (total volume fraction in the range 10–15% at the beginning of the simulation). This shows that the corrections to the outflux deriving from the mass balance in the box work perfectly. We checked that the model behavior is still correct with volume fractions in the gas phase up to 50% or higher (not shown). We also check again that the drying kinetics is independent of the LV interface profile, and hence of the parameters \( \kappa_i \) and \( \varepsilon_{vap} \) as well as of \( M_{vap} \) provided it is high enough (not shown).
The evaporation rate is time-dependent because it is composition-dependent, and the film composition varies with time. Therefore, the evolution of the film composition should be correct, as shown in Figure 9. Beyond the drying kinetics, this might be crucial for the proper simulation of the film structuration. For example, critical processes such as liquid–liquid phase separation or nucleation are only triggered from a given composition in the film. Once again, the agreement between theory and simulation is excellent.

In practical situations, solvent blending is known as a powerful tool in order to monitor the structuration of the drying film. The blend is often chosen depending on criteria such as the interactions with the various solutes, their wetting properties, and their individual evaporation rates. However, for a solvent blend, the evaporation kinetics and the composition of the drying film have a nontrivial time evolution, depending on the molar volumes, densities, and vapor pressures of the individual solvents. This in turn can also have an influence on the film structuring and should be taken into account for an optimal choice of the solvent blend. We hope that this kind of model can help such considerations.

Evaporation of Fluid Mixtures: Solute Deposition. Toward deposition of solution-processed thin films, we finally investigate the case of a drying mixture containing one solvent and one solute. The three fluids in the simulation are the solute, the solvent, and the air, as described earlier. We only study the impact of the solution thermodynamics on the time dependence of the evaporation rate. In order to do so, we perform simulations at low Biot numbers. The Biot number $B_i$ is

$$B_i = \frac{d_{ref}}{L_i} \cdot \frac{\rho_i \cdot \frac{d_{ref}^2}{2} \cdot v_i}{k_i}.$$ 

Figure 9. Volume fraction of the second solvent in the liquid film during evaporation of a binary blend for various parameters for the second solvent and the interaction parameter. For the 1st solvent, $N = 3$ and $\phi_{sat} = 0.028$. Theory, eqs 26–28, (full lines) and simulation (symbols).

Figure 10. Typical volume fraction field for the solute (a), the solvent (b), the air (c), and order parameter field (d) during drying. The interface moves from right to left from the initial state (blue) to the final state (brown). The system is discretized by 2048 points.
ensure Bi time-dependence of the evaporation rate and is deliberately avoided here. However, this purely kinetic effect will be illustrated later in this paper on the case of a PS–toluene mixture.

The typical field evolution in such a simulation is shown in Figure 10. The solvent volume fraction in the vapor phase is once again homogeneous and decreases with time. The volume fraction field in the liquid film is also homogeneous, except at the film surface. The brown curve shows the final, dry state, which does not change further with time. The solvent volume fraction peak is not due to the kinetic effect described above, the Biot number in our simulation being below $10^{-3}$, but this is simply the equilibrium profile of the LV interface. It is due to the fact that the solvents have much higher vapor pressures than the solutes and thus preferentially occupy the interface. The height of the peak is at first order determined by the ratio of the vapor pressures of the solvent and the solute. We are not sure that this peak is physical but it could make sense that solvent molecules preferentially gather at the very surface before/while undergoing the LV phase transition. Luckily, as already stated several times above, the interface profile has no impact on the kinetics, except the following small bias: the interface (and hence the peak) is unrealistically broad in order to allow for numerically tractable simulations. As a result, coming closer and closer to the dry state, the amount of solvent contained in this region might become important compared to the amount in the bulk liquid film. This might result in slightly modified equilibrium compositions and differences between simulation and theory. Simply increasing the box size can solve this problem so that the volume at the interface becomes negligible compared to the volume in the bulk. For this reason, we performed solute deposition simulations with 2048 grid points, leading to a final film height of 180 nm, as shown in Figure 10. The fields for the case with 512 grid points (final height of 45 nm) are shown in the Supporting Information (S3) for comparison.

Here again, we analyze the time-dependence of the evaporation rate for various parameters and compare it to the theoretical results obtained with the method detailed in the previous paragraph (Figure 11). The time-dependence of the liquid film composition, which is the reason for the changes in the drying rate, has also been analyzed (Figure 12). Once again, the agreement between the theory and the experiment is very good. For the ideal mixture (black curve), the evaporation rate decreases very smoothly and the equation of the curve can be derived analytically. The more incompatible the solute and the solvent are and the bigger the solute molecules are, the more constant is the evaporation rate. This can be qualitatively understood going back to Figure 2. For high interaction parameters and different molecular sizes, the solubility curve of the smaller component is shifted so that the equilibrium partial pressure of the solvent becomes almost constant for a broad range of volume fractions in the liquid film and, therefore, for a long period of the drying process in the simulation.

This is expected to be a general phenomenon and leads to the conclusion that for a given solvent, this thermodynamic effect pushes the evaporation rate of a polymer solution to be much more constant than the one of a small molecule solution. This produces the so-called “constant rate” drying phase of polymer solutions. However, the low diffusion coefficients at high polymer concentrations at the end of the drying might lead to a high Biot number and strong concentration gradients in the film. The kinetic effect becomes dominant as compared to the thermodynamic effect, and the drying rate can drop over several orders of magnitudes. Similarly, poorly compatible solutions should tend to evaporate at a more constant rate, at least as long as they stay miscible and that no liquid–liquid phase separation is triggered.

Comparison with Experimental Results in the Case of PS–Toluene Solutions. For a quantitative illustration, we simulate the experiments of drying polystyrene–toluene
solutions reported in our previous work.26 The parameters for toluene are taken from Hansen’s solvent database.60 The experiments were performed at room temperature (20 °C), and films of about 2 μm dry thickness were produced. The molecular weight of the linear PS is very good and demonstrates the quantitative accuracy of between experimental and simulation results, shown in Figure 13, is very good and demonstrates the quantitative accuracy of

The Biot number is of the order of 0.01 at the beginning of the drying and the thermodynamic effect is dominant; the evaporation rate is almost constant, due to the high molecular weight of the polymer compared to the solvent, and drops suddenly at the end of the drying as expected from the LV equilibrium. At the same time, when the volume fraction of solvent has reached roughly 50%, the Biot number gets close to 1 and concentration gradients appear in the film (see S4 in Supporting Information). This leads to a polymer skin at the top of the film with very slow diffusion so that when the remaining solvent volume fraction reaches about 10%, the drying rate decreases by more than one order of magnitude. Note that we cannot observe this second phase of slow drying in the experiments, which end shortly after the end of the “constant rate” phase. Unfortunately, we do not have any means of evaluating the residual solvent quantity at the end of the measurements, but the films might not be fully dry. Because we expect this huge slow down when the volume fraction of solvent reaches 10%, we assume the residual solvent quantity in the experiments to be 10% for the sake of the comparison with the simulation. The behavior at longer times (until the complete drying in the simulation) is shown in S4 in Supporting Information. Because the measurements are performed below the glass transition temperature of the blend at a low solvent concentration (roughly below 10–15%),38 we expect an impact of the relaxation kinetics that can further slow down the drying kinetics. However, we cannot observe such an effect, probably because the measurement time is not sufficient.

Example of 2D Simulations with Surface Deformation. One of the key features of our framework is that the LV interface is located inside the simulation box. This allows for the tracking of its position without any further changes to the model, even if the interface deforms or bends. In particular, no remeshing technique is required, and a simple fixed, rectangular, regular mesh can be used. To illustrate this feature, we perform 2D simulations of a drying solvent–solute binary blend on a rough substrate (see Figure 14). We use a

| h/I | \( \phi_0 = 0.9 \) | \( \phi_0 = 0.8 \) | \( \phi_0 = 0.7 \) | \( \phi_0 = 0.6 \) |
|-----|-----------------|-----------------|-----------------|-----------------|
| 0   | 0.9             | 0.8             | 0.7             | 0.6             |
| 0.5 | 0.8             | 0.7             | 0.6             | 0.5             |
| 1   | 0.7             | 0.6             | 0.5             | 0.4             |
| 1.5 | 0.6             | 0.5             | 0.4             | 0.3             |

Figure 13. Simulated time-dependent film height (symbols) for different volume fractions \( \phi_0 \) of solvent in the initial film and comparison to the experimental results (full lines, reproduced from ref26 with permission from the PCCP Owner Societies) for a 35 kg/mol PS–toluene mixture. Error bars represent ±1 standard deviation. \( h_0 \) is the initial height, and \( r \) is the time needed to dry a film with \( \phi_0 = 0.9 \) at a constant drying rate.

The grid spacing has been chosen to be 10 nm; we adjusted \( k = 6 \times 10^{-9} \) (J/m) and \( \varepsilon_{\text{evap}} = 9 \times 10^{-4} \) (J/m)\(^{0.5} \) in order to have a sufficiently broad LV interface. The agreement between experimental and simulation results, shown in Figure 13, is very good and demonstrates the quantitative accuracy of the phase-field simulation framework presented in this paper. The Biot number is of the order of 0.01 at the beginning of the drying and the thermodynamic effect is dominant; the evaporation rate is almost constant, due to the high molecular weight of the polymer compared to the solvent, and drops suddenly at the end of the drying as expected from the LV equilibrium. At the same time, when the volume fraction of solvent has reached roughly 50%, the Biot number gets close to

Figure 14. Initial (light blue) and final positions of the film surface after drying of a solute–solvent mixture on a rough substrate. The final state of different simulations with initial solute volume fractions varying from \( \phi_0 = 0.8 \) (dark blue) to \( \phi_0 = 0 \) (red) is shown. The substrate surface is indicated by the dashed black line.

regular 256*128 mesh with a grid spacing of 2 nm (the detailed parameters of the simulation are given in S5 in Supporting Information). Two structures of different heights are present on the substrate. Several simulations with an initial solute volume fraction varying from 0 to 0.8 are performed. For the highest solute volume fractions (\( \phi_0 = 0.8 \) and \( \phi_0 = 0.6 \)), the dry film fully covers both structures. For \( \phi_0 = 0.4 \), it can be seen that the interface bends around the highest structure so that the dry film is not completely flat. For \( \phi_0 = 0.2 \),
0.2, the interface bends around both substrate structures. Finally, for \( q_0 = 0 \) (pure solvent drying), the substrate is fully dewetted and the final interface follows the substrate morphology. Note that in that case, dewetting in the flat area between both structures occurs before the end of the drying so that the LV interface separates into two distinct parts (not shown). This demonstrates the potential of our framework to handle different situations where surface deformation has to be taken into account. Not only drying on structured and rough substrates can be considered but also any kind of situation where the morphology formation during drying might lead to interface deformations or even to a rough film (for instance during drying of immiscible polymer mixtures\(^\text{64}\) or crystallizing films). This will be the topic of intensive future work.

**CONCLUSIONS AND PERSPECTIVES**

In this work, we developed a phase-field simulation framework that mimics the Hertz–Knudsen description of evaporation processes. The fast interfacial mobility used in the Allen–Cahn equation ensures a quasi-static equilibrium between the liquid phase and the vapor phase close to the film surface. The diffusion of gas molecules away from the film surface is modeled with a flux boundary condition that recovers the Hertz–Knudsen relationship for the evaporation rate of a pure solvent. The solvent surface tension is also successfully reproduced. For fluid mixtures, the simple situation where the drying is not influenced by gas phase resistances, limited diffusion in the liquid film, or polymer relaxation has been investigated. Our evaporation procedure generates drying curves in excellent agreement with the theoretical results that can be expected from the LV equilibrium calculated with the Flory–Huggins theory. The simulations have also been successfully compared to experimental data obtained in such a simple case, and we obtained a nice alignment of simulation, theory, and measurements. The simulation framework can handle surface deformation and hence film roughness without any further modification, as has been exemplified in 2D simulations of drying on a rough substrate.

In this paper, in order to test the validity of the phase-field model, we showed simulations of the very simple situation where the LV equilibrium together with the Hertz–Knudsen approach is responsible for the drying kinetics. However, in real systems, as detailed before, other physical processes may play an important role and the model can be improved in several ways to take them into account:

- Because we used a simple Hertz–Knudsen theory for pure solvent evaporation, our simulations inherit from all its advantages but also from its imperfections documented by comparisons with experimental results. We believe that this could be improved in a straightforward manner by implementing the progress made on the Hertz–Knudsen theory\(^\text{29,32,36,37}\) in the formula for the flux at the boundary.

- Similarly, the role of the processes in the gas phase (Stefan flow and forced laminar or even turbulent convection) can be integrated by simply making the coefficient \( \alpha \), or more generally the expression of the outflux (eq 18), dependent on the nature and intensity of the gas flow using classical phenomenological descriptions like Sherwood correlations.\(^\text{65}\)

- For the evaporation kinetics of solvent and polymer mixtures, potential deviations from experiments could be associated with the accuracy of the Flory–Huggins theory and corrected easily by an improved description of the thermodynamics of the liquid solution (typically composition-dependent interaction parameters and other forms for the excess energy of mixing such as the Redlich–Kistler extension\(^\text{45}\)).

- For film drying simulations, our model predicts solvent accumulation in the LV interface. Whether this accumulation is physical or just a consequence of the diffuse interface approach, as well as the consequences on the simulation results, are questions that should be addressed in the near future.

In the future, such an improved model could be cross-checked with already available exhaustive data. However, it has already been shown that these situations could be successfully calculated in the 1D case.\(^\text{32,56,57}\) In fact, the benefits of such a tool become clear in much more complex situations. Possible examples of these complex situations are mixtures of four and five or more fluids, which is after all quite common in the solution processing of thin films. Because our framework is readily written for any number of components in the mixtures, such systems could be in principle simulated without any further modifications of the governing equations. Other examples are films where evaporation-induced phase transformation (spinodal decomposition, crystallization, etc.) takes place and leads to strong inhomogeneity and time-dependence of the film properties. An example of a practical application is solution-processed organic photoactive layers, for which both aspects of complexity are relevant. The numerically efficient implementation of the code allows for heavy 2D/3D simulations of such situations. This will be demonstrated in future work, coupling the equations presented here with previous work.\(^\text{66}\)

To the best of our knowledge, the existing simulation procedures used to study the structure formation upon drying in two or three dimensions most often describe only the liquid film and set an outflux at the upper surface of the film. This outflux is sometimes assumed to be constant\(^\text{16}\) or proportional to the liquid volume fraction at the surface.\(^\text{16}\) In this context, we believe that the best solution is the one proposed by Dehsari and co-workers where the solvent partial pressures are calculated as \( P_{\text{sat}}e^{\mu/RT} \), which produces in fact the same evaporation flux as compared to our approach. This should lead to more accurately simulated drying kinetics, drying times, and therefore final morphologies, and beyond this to a better understanding of the dry film properties. Nevertheless, we believe that our model brings one interesting feature: even by using a simple, regular fixed mesh, the film surface deformation can be tracked and effects such as roughness formation or incomplete substrate coverage can be accounted for, similar to what has been already demonstrated.\(^\text{26,64}\) This will be of the highest importance for the simulation of film drying on rough substrates, as well as for situations where the morphology formation during evaporation results in rough dry films. This can typically be the case when liquid–liquid phase separation occurs in polymer systems or when crystallization processes occur during drying. For example, this is a well-known problem for the quality of the photoactive layer in perovskite solar cells.\(^\text{69,70}\)
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