PHYSICAL REVIEW E **80**, 021606 (2009)

Nonequilibrium thermodynamics of transport through moving interfaces with application to bubble growth and collapse

Hans Christian Öttinger[*]
Department of Materials, Polymer Physics, ETH Zürich, HCI H 543, CH-8093 Zürich, Switzerland

Dick Bedeaux[†]
Department of Chemistry, Norwegian University of Science and Technology, Trondheim 7491, Norway
and Department of Process and Energy, Technical University of Delft, Leeghwaterstraat 44, 2628 CA Delft, The Netherlands

David C. Venerus[‡]
Department of Chemical & Biological Engineering, Illinois Institute of Technology, 10 West 33rd Street, Chicago, Illinois 60616, USA

(Received 23 March 2009; published 21 August 2009)

We develop the general equation for the nonequilibrium reversible-irreversible coupling framework of thermodynamics to handle moving interfaces in the context of a gas that can be dissolved in a surrounding liquid. The key innovation is a "moving interface normal transfer" term required for consistency between the thermodynamic evolution equation and the chain rule of functional calculus. The freedom of atomistic displacements of the interface leads to gauge transformations under which the thermodynamic theory should be invariant. The thermodynamic framework provides a complete set of evolution equations and boundary conditions, as we illustrate for the example of bubble growth and collapse.

DOI: 10.1103/PhysRevE.80.021606 PACS number(s): 68.03.−g, 05.70.Np, 05.70.Ln, 68.35.Md

I. INTRODUCTION

In the description of transport through, into, and along interfaces using nonequilibrium thermodynamics, one may use excess densities, fluxes, and also structural variables at the so-called dividing surface. For equilibrium systems, there are only excess densities. A systematic analysis of the equilibrium properties of surfaces using excess densities was first given by Gibbs [1]. In 1967, Waldmann [2] made a first step to describe transport in the presence of surfaces. He calculated the excess entropy production and was able to formulate boundary conditions. In 1976, Bedeaux *et al.* [3] extended the work of Waldmann and included the thermodynamic excess densities considered by Gibbs. This was the beginning of a whole series of papers (see, for example, [4,5]). Essential in the method in these papers is the use of generalized functions for the various densities and fluxes. From one phase to the other, these densities and fluxes change discontinuously and, in addition to that, they have singular contributions on the dividing surface. This implies the use of Heaviside and delta functions. While this may seem complicated, it—in practice—provides an efficient and elegant method to keep track of everything that moves in the neighborhood of the surface, including the motion of the surface itself.

It is the goal of this paper to develop the more recent "general equation for the nonequilibrium reversible-irreversible coupling" (GENERIC) [6–8] so that it can handle the thermodynamic description of moving interfaces. This requires a coupled description of two- and three-dimensional subsystems. GENERIC goes beyond classical nonequilibrium thermodynamics in that it is not restricted to linear relations between thermodynamic fluxes and forces. It extends the classical theory in this way and gives a convincing generalization of the Onsager relations to the nonlinear regime. Previous work on boundary thermodynamics in the GENERIC framework [9–11] is here generalized to a consistent description of moving interfaces.

The present paper contains three major contributions: (i) A moving interface normal transfer (MINT) term is introduced to obtain consistency between the fundamental thermodynamic evolution equation and the chain rule of functional calculus. (ii) It is elaborated that thermodynamic theories with interfaces have the character of gauge theories, where the gauge transformations are related to macroscopically irrelevant atomistic displacements of the interface. (iii) The theoretical developments are illustrated by applying them to the problem of bubble growth and collapse without equilibrium at the interface, which is an interesting problem in its own right.

The growth and collapse of gas bubbles in liquids driven by mass diffusion occurs in natural, biological, and technological systems. For example, the growth of bubbles in volcanic magmas [12], the collapse of gas bubbles in biological fluids [13], and the growth of bubbles in polymeric foam production [14]. Not surprisingly, many studies have been conducted in order to develop transport models that allow the prediction of bubble growth and collapse rates. The existence of a moving interface, which couples mass and momentum transfer between the gas and liquid phases, gives these phenomena a rich dynamic behavior.

Diffusion-controlled bubble growth and collapse has been studied extensively. The term diffusion-*controlled* describes systems where hydrodynamic effects can be neglected and the pressure within the bubble is constant. Numerical solutions for diffusion-controlled bubble growth and collapse, where the difficulties of a moving boundary, steep concen-

---

[*] hco@mat.ethz.ch; www.polyphys.mat.ethz.ch

[†] dick.bedeaux@chem.ntnu.no

[‡] venerus@iit.edu

tration gradients, and a semi-infinite domain encountered in this problem, have been reported by Duda and Vrentas [15,16]. For the case of bubble growth from a zero initial radius, an exact solution based on similarity transformation has been found [17].

Transport models for diffusion-*induced* bubble growth and collapse in viscous liquids involve additional and sometimes subtle effects not found in the governing equations for diffusion-controlled phenomena. In most of previous work, one or more approximations have been invoked. One of these is the well-known thin boundary approximation, which assumes that variations in the concentration of the diffusing species are confined to a thin region in the liquid surrounding the bubble. A second approximation exploits the fact that the ratio of the gas phase to liquid phase density is typically small. The earliest model for diffusion-induced bubble growth appears to be that of Barlow and Langlois [18], who used both approximations described above. The dissolution of a gas bubble in viscoelastic liquids was modeled by Zana and Leal [19]. More recently, the ranges of validity of these approximations were established by Venerus and Yala [20] for bubble growth in Newtonian liquids and by Venerus *et al.* [21] for bubble growth in viscoelastic liquids.

We are interested in the growth and dissolution of a gas bubble surrounded by a liquid containing dissolved gas. All previous analyses of diffusion-induced bubble growth and collapse are based on equations for the bulk phases and for the interface (so-called "jump balances") derived using traditional approaches in hydrodynamics [22,23]. In addition, the relationship between the concentration of the diffusing species in the gas and liquid phases is based on the assumption of thermodynamic equilibrium at the interface.

We look for a thermodynamic description of the evolution of a system in which, in addition to bulk fields in the gas and liquid phases, there are fields defined only in the two-dimensional interface to account for relevant interfacial properties [9,10]. The interfacial layer is not necessarily unresolvable by experimental methods; we might merely refrain from looking at it in more detail if, for example, just the bubble size is of interest. This phenomenological thermodynamic approach is elaborated in this paper. Some of the equations developed here may look a bit lengthy. However, one should keep in mind that a single equation (GENERIC) contains all the information about the system: the hydrodynamic equations for the gas, the hydrodynamic equations for the two-component liquid, the interfacial hydrodynamics, and all the required boundary conditions. Some of the resulting evolution equations and boundary conditions do not seem to be immediately obvious.

II. SYSTEM AND THERMODYNAMICS

One of the goals of this work is to formulate the evolution of a system with interfaces within a thermodynamic system. The first step is to define a thermodynamic system, that is, to choose the variables x in terms of which a complete and self-contained description of all phenomena of interest is possible. The second step is to formulate the thermodynamic building blocks required for constructing evolution equations as functions of the system variables x. In the GENERIC framework of nonequilibrium thermodynamics [6–8], these building blocks are the energy $E(x)$, the entropy $S(x)$, the Poisson bracket that translates the gradient of $E(x)$ into reversible motion, and the dissipative bracket that translates the gradient of $S(x)$ into irreversible motion.

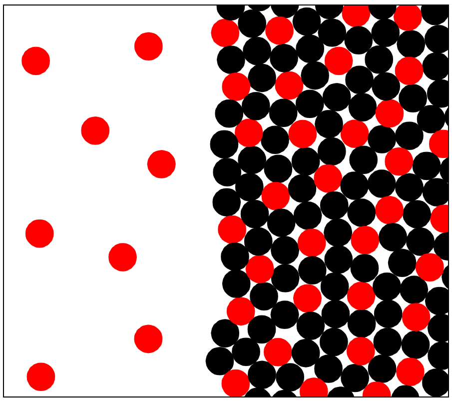

FIG. 1. (Color online) Gas-liquid interface showing boundary layer with bulk composition.

A. System variables

We choose separate lists of variables for describing the two bulk phases and the separating interface:

(i) To describe the bulk gas phase in the domain V^{g}, we use the hydrodynamic fields mass, momentum, and internal energy density $x^{\mathrm{g}}=(\rho^{\mathrm{g}},\boldsymbol{M}^{\mathrm{g}},\epsilon^{\mathrm{g}})$.

(ii) To describe the bulk liquid phase in the domain V^{l}, we use the hydrodynamic fields $x^{\mathrm{l}}=(\rho^{\mathrm{l}},\boldsymbol{M}^{\mathrm{l}},\epsilon^{\mathrm{l}},c^{\mathrm{l}})$, where the additional variable c^{l} is the mass fraction of solute in the two-component liquid.

(iii) To describe the interface I between V^{g} and V^{l}, we use $x^{\mathrm{s}}=(\rho^{\mathrm{s}},\boldsymbol{M}^{\mathrm{s}},\epsilon^{\mathrm{s}})$, where ρ^{s} is the excess mass in the interfacial layer, $\boldsymbol{M}^{\mathrm{s}}$ is the excess momentum, and ϵ^{s} is the excess internal energy.

It is natural to introduce the variables ρ^{s} and $\boldsymbol{M}^{\mathrm{s}}$ because, as a consequence of the exchange of mass through the interface, the velocity of the interface $\boldsymbol{v}^{\mathrm{s}}=\boldsymbol{M}^{\mathrm{s}}/\rho^{\mathrm{s}}$ differs from the gas and solution velocities. The mass fraction of solute in the interface c^{s} is assumed to be equal to c^{l} in the bulk solution near the interface. This simple situation is illustrated in a naive manner in Fig. 1; a much deeper discussion is given at the end of the following subsection on gauge invariance. In general, the composition in the interface may clearly be different from the bulk composition. For a clear distinction of the three subsystems and for the treatment of the interface as an autonomous system in its own right (with suitable local-equilibrium states), it would clearly be preferable to keep c^{s} and c^{l} as separate variables and, whenever this is a physically meaningful approximation, to impose the condition $c^{\mathrm{s}}=c^{\mathrm{l}}$ as a constraint. Although there exists a straightforward and rigorous procedure for incorporating constraints into the GENERIC framework [24], we here prefer to avoid a separate variable c^{s} to focus on the problems associated with moving interfaces and to avoid the general framework of constraints.

In the same spirit, we make the simplifying assumption that there are no solvent particles in the gas phase.

B. Gauge invariance

It has been observed that there are two kinds of variables in interfaces (see discussion in Sec. 4 of [25]). Variables of the first kind are insensitive to the precise location of the interface, whereas variables of the second kind change significantly even if the interface is relocated only by atomic distances. To simplify the discussion, we distinguish between macroscopically relevant and ambiguous variables. By a suitable definition of the precise interface location, one can typically make an ambiguous excess variable vanish, as has been known since the pioneering work of Gibbs on dividing surfaces [1]. One might hence be tempted to eliminate all ambiguous variables, but this may lead to serious problems because different locations of the interface are required to eliminate the various ambiguous variables.

It may be better to treat the freedom of the precise location of the interface as a gauge degree of freedom within a continuum field theory of hydrodynamics. If one chooses one of the ambiguous interface variables to be zero, all the other ambiguous variables are fixed but may be nonzero. If we arbitrarily change one of the ambiguous variables, all other variables must be changed according to certain gauge transformations. For a functional of the general form,

$$A = \int_{V^{\mathrm{g}}} a^{\mathrm{g}}(x^{\mathrm{g}})d^3r + \int_{V^{\mathrm{l}}} a^{\mathrm{l}}(x^{\mathrm{l}})d^3r + \int_I a^{\mathrm{s}}(x^{\mathrm{s}},x^{\mathrm{g}},x^{\mathrm{l}})d^2r, \quad (1)$$

where we allow the occurrence of x^{g} and x^{l} in a^{s} as a consequence of constraints introduced to simplify the description of the system, the gauge transformation associated with an atomistic displacement ℓ of the interface changes the interfacial excess density variable a^{s} according to the law,

$$a^{\mathrm{s}} \to a^{\mathrm{s}} + \ell(a^{\mathrm{g}} - a^{\mathrm{l}}), \quad (2)$$

where we have neglected curvature effects [see Eq. (40) below]. Only for quantities varying slowly through the interfacial region ($a^{\mathrm{g}} \approx a^{\mathrm{l}}$), the interfacial contribution can vanish independently of the precise location of the interface. For a relevant interfacial variable, $a^{\mathrm{s}} \gg \ell(a^{\mathrm{g}} - a^{\mathrm{l}})$ for all displacements on the order of the interface thickness so that a^{s} indeed remains unaffected by gauge transformations. The physical predictions of the continuum theory should be independent of the choice of the gauge. While the physical origin of the gauge freedom lies in the importance of displacements of the interface by atomic distances, from a continuum perspective, it appears as a formal invariance under the class of gauge transformations [Eq. (2)]. The discussion of the field theory should hence include the investigation of the invariance of the physical predictions under gauge transformations.

Among our interfacial variables x^{s}, we expect ρ^{s} and $\boldsymbol{M}^{\mathrm{s}}$ to be ambiguous and, in the presence of interfacial tension, ϵ^{s} to be relevant. In view of the relationship $\boldsymbol{M}^{\mathrm{s}} = \rho^{\mathrm{s}}\boldsymbol{v}^{\mathrm{s}}$, however, it is natural to assume that, although the interfacial mass and momentum densities are small and ambiguous, the ratio $\boldsymbol{v}^{\mathrm{s}}$ is a finite and relevant interfacial variable characterizing the motion of and along the interface. Gauge invariance of $\boldsymbol{v}^{\mathrm{s}}$ under the transformations in Eq. (2) of ρ^{s} and $\boldsymbol{M}^{\mathrm{s}}$ requires the following condition:

$$\boldsymbol{v}^{\mathrm{s}} = \frac{\boldsymbol{M}^{\mathrm{s}}}{\rho^{\mathrm{s}}} = \frac{\boldsymbol{M}^{\mathrm{l}} - \boldsymbol{M}^{\mathrm{g}}}{\rho^{\mathrm{l}} - \rho^{\mathrm{g}}}, \quad (3)$$

which plays the role of a boundary condition. In words, the dividing interfaces for mass and momentum must coincide; a massless interface cannot carry any momentum. Note that, in general, $\boldsymbol{v}^{\mathrm{s}}$ is unequal to both $\boldsymbol{v}^{\mathrm{g}} = \boldsymbol{M}^{\mathrm{g}}/\rho^{\mathrm{g}}$ and $\boldsymbol{v}^{\mathrm{l}} = \boldsymbol{M}^{\mathrm{l}}/\rho^{\mathrm{l}}$.

The idea of gauge invariance is closely related to the subtle concept of local equilibrium in an interface. To what extent can the interfacial variables be independent of the properties of the surrounding bulk phases in contact with the interface? For example, (how) can one have three different temperatures in the interface and in the two bulk phases in an infinitesimal neighborhood of the interface? The idea of an autonomous interface in nonequilibrium systems was established in [26] from an underlying more detailed square gradient model for the interface. In Sec. 6 of [26], it has been shown that under local-equilibrium conditions, differences of the type $a^{\mathrm{g}} - a^{\mathrm{l}}$ must have the same value as under global equilibrium conditions with the same state of the interface. The verification of the local-equilibrium idea for two-component systems has been performed recently [27]. This observation leads to the gauge invariance of the intensive thermodynamic state variables characterizing the interface, such as the temperature and the chemical potential, in addition to the gauge invariance of the interface velocity.

The arguments for clarifying the role of the surface composition c^{s} are very similar to those for the surface velocity $\boldsymbol{v}^{\mathrm{s}}$. Like the excess of the total mass, we expect the excess of the gas/solute species to be an ambiguous quantity. By analogy with Eq. (3), we formulate a gauge invariance condition of the form

$$c^{\mathrm{s}} = \frac{c^{\mathrm{l}}\rho^{\mathrm{l}} - \rho^{\mathrm{g}}}{\rho^{\mathrm{l}} - \rho^{\mathrm{g}}} \quad (4)$$

to establish the mass fraction c^{s} as a relevant variable. To justify the assumption $c^{\mathrm{s}} = c^{\mathrm{l}}$, we need to assume that not only the solution density is large compared to the gas density but even the solute density. This situation is suggested in Fig. 1, where the solute density is visibly larger than the gas density. Whether or not such an assumption is realistic depends on the nature of the gas and the solvent of interest.

A common way of characterizing the solubility of a gas in a liquid is by giving the constant in Henry's law as the ratio $k_{\mathrm{H,cc}}$ of the solute to gas densities. For $k_{\mathrm{H,cc}} \gg 1$, the simplifying assumption $c^{\mathrm{s}} = c^{\mathrm{l}}$ is justified. For example, for carbon dioxide in water, $k_{\mathrm{H,cc}}$ at room temperature is on the order of unity, so that $c^{\mathrm{s}} \neq c^{\mathrm{l}}$. For sulfur dioxide in water at room temperature or carbon dioxide in polystyrene at elevated temperatures, on the other hand, $k_{\mathrm{H,cc}}$ is on the order of 30 or around 10, respectively, so that $c^{\mathrm{s}} = c^{\mathrm{l}}$ is a reasonable assumption. In other situations, the simplifying assumption $c^{\mathrm{s}} = c^{\mathrm{l}}$ should be replaced by Eq. (4), resulting from gauge invariance, or the simpler version for $\rho^{\mathrm{g}} \ll \rho^{\mathrm{l}}$,

$$c^{\mathrm{s}} = c^{\mathrm{l}} - \frac{\rho^{\mathrm{g}}}{\rho^{\mathrm{l}}}. \tag{5}$$

Note that a positive sign of c^{s} can only be expected for $k_{\mathrm{H,cc}} > 1$.

C. Energy and entropy

We begin our construction of the thermodynamic building blocks for our two-phase system with interfaces by formulating the energy

$$E = \int_{V^{\mathrm{g}}} \left(\frac{\boldsymbol{M}^{\mathrm{g}^2}}{2\rho^{\mathrm{g}}} + \epsilon^{\mathrm{g}} \right) d^3r + \int_{V^{\mathrm{l}}} \left(\frac{\boldsymbol{M}^{\mathrm{l}^2}}{2\rho^{\mathrm{l}}} + \epsilon^{\mathrm{l}} \right) d^3r + \int_I \left(\frac{\boldsymbol{M}^{\mathrm{s}^2}}{2\rho^{\mathrm{s}}} + \epsilon^{\mathrm{s}} \right) d^2r, \tag{6}$$

and the entropy

$$S = \int_{V^{\mathrm{g}}} s^{\mathrm{g}}(\rho^{\mathrm{g}}, \epsilon^{\mathrm{g}}) d^3r + \int_{V^{\mathrm{l}}} s^{\mathrm{l}}(\rho^{\mathrm{l}}, \epsilon^{\mathrm{l}}, c^{\mathrm{l}}) d^3r + \int_I s^{\mathrm{s}}(\epsilon^{\mathrm{s}}) d^2r. \tag{7}$$

Note that, for simplicity, we have assumed that the interfacial contribution to the entropy is independent of the composition of the liquid in the boundary layer. Otherwise, we should introduce c^{s} as an additional interfacial variable. It is natural to introduce the subsystem temperatures

$$\frac{1}{T^{\mathrm{g}}} = \frac{\partial s^{\mathrm{g}}}{\partial \epsilon^{\mathrm{g}}}, \quad \frac{1}{T^{\mathrm{l}}} = \frac{\partial s^{\mathrm{l}}}{\partial \epsilon^{\mathrm{l}}}, \quad \frac{1}{T^{\mathrm{s}}} = \frac{\partial s^{\mathrm{s}}}{\partial \epsilon^{\mathrm{s}}}. \tag{8}$$

It will be useful to look at the expressions for the total mass,

$$M^{\mathrm{tot}} = \int_{V^{\mathrm{g}}} \rho^{\mathrm{g}} d^3r + \int_{V^{\mathrm{l}}} \rho^{\mathrm{l}} d^3r + \int_I \rho^{\mathrm{s}} d^2r, \tag{9}$$

and for the mass of the gas and solute species,

$$M^{\mathrm{g/s}} = \int_{V^{\mathrm{g}}} \rho^{\mathrm{g}} d^3r + \int_{V^{\mathrm{l}}} c^{\mathrm{l}} \rho^{\mathrm{l}} d^3r + \int_I c^{\mathrm{l}} \rho^{\mathrm{s}} d^2r, \tag{10}$$

because their degeneracy (expressing unconditional mass conservation) is a useful guideline for the formulation of dissipative processes at the interface. For the observable $M^{\mathrm{g/s}}$, the interfacial contribution actually depends on a bulk variable (because we have used the condition $c^{\mathrm{s}} = c^{\mathrm{l}}$ to reduce the number of system variables rather than as a constraint), as allowed for the general form of functionals given in Eq. (1).

D. Poisson bracket

The Poisson bracket of two observables A and B (that is, functionals of the thermodynamic variables x^{g}, x^{l}, and x^{s}; examples are given by E, S, M^{tot}, and $M^{\mathrm{g/s}}$) is assumed to consist of separate well-known bulk contributions and a similar interfacial contribution

$$\{A,B\} = \{A,B\}^{\mathrm{g}} + \{A,B\}^{\mathrm{l}} + \{A,B\}^{\mathrm{s}}, \tag{11}$$

with the standard bracket of hydrodynamics for the gas phase in the manifestly antisymmetric form [8,28],

TABLE I. Examples of $\tilde{a}^{\mathrm{g}}$.

a^{g}	$\tilde{a}^{\mathrm{g}}$
ρ^{g}	ρ^{g}
$\boldsymbol{M}^{\mathrm{g}}$	$\boldsymbol{M}^{\mathrm{g}}$
ϵ^{g}	$\epsilon^{\mathrm{g}} + p^{\mathrm{g}}$
s^{g}	s^{g}

$$\begin{aligned}
\{A,B\}^{\mathrm{g}} = &- \int_{V^{\mathrm{g}}} \rho^{\mathrm{g}} \left(\frac{\partial a^{\mathrm{g}}}{\partial \boldsymbol{M}^{\mathrm{g}}} \cdot \frac{\partial}{\partial \boldsymbol{r}} \frac{\partial b^{\mathrm{g}}}{\partial \rho^{\mathrm{g}}} - \frac{\partial b^{\mathrm{g}}}{\partial \boldsymbol{M}^{\mathrm{g}}} \cdot \frac{\partial}{\partial \boldsymbol{r}} \frac{\partial a^{\mathrm{g}}}{\partial \rho^{\mathrm{g}}} \right) d^3r \\
&- \int_{V^{\mathrm{g}}} \boldsymbol{M}^{\mathrm{g}} \cdot \left(\frac{\partial a^{\mathrm{g}}}{\partial \boldsymbol{M}^{\mathrm{g}}} \cdot \frac{\partial}{\partial \boldsymbol{r}} \frac{\partial b^{\mathrm{g}}}{\partial \boldsymbol{M}^{\mathrm{g}}} - \frac{\partial b^{\mathrm{g}}}{\partial \boldsymbol{M}^{\mathrm{g}}} \cdot \frac{\partial}{\partial \boldsymbol{r}} \frac{\partial a^{\mathrm{g}}}{\partial \boldsymbol{M}^{\mathrm{g}}} \right) d^3r \\
&- \int_{V^{\mathrm{g}}} \epsilon^{\mathrm{g}} \left(\frac{\partial a^{\mathrm{g}}}{\partial \boldsymbol{M}^{\mathrm{g}}} \cdot \frac{\partial}{\partial \boldsymbol{r}} \frac{\partial b^{\mathrm{g}}}{\partial \epsilon^{\mathrm{g}}} - \frac{\partial b^{\mathrm{g}}}{\partial \boldsymbol{M}^{\mathrm{g}}} \cdot \frac{\partial}{\partial \boldsymbol{r}} \frac{\partial a^{\mathrm{g}}}{\partial \epsilon^{\mathrm{g}}} \right) d^3r \\
&- \int_{V^{\mathrm{g}}} \left[\frac{\partial a^{\mathrm{g}}}{\partial \boldsymbol{M}^{\mathrm{g}}} \cdot \frac{\partial}{\partial \boldsymbol{r}} \left(p^{\mathrm{g}} \frac{\partial b^{\mathrm{g}}}{\partial \epsilon^{\mathrm{g}}} \right) - \frac{\partial b^{\mathrm{g}}}{\partial \boldsymbol{M}^{\mathrm{g}}} \cdot \frac{\partial}{\partial \boldsymbol{r}} \left(p^{\mathrm{g}} \frac{\partial a^{\mathrm{g}}}{\partial \epsilon^{\mathrm{g}}} \right) \right] d^3r,
\end{aligned} \tag{12}$$

where p^{g} is the pressure in the gas given by

$$p^{\mathrm{g}} \frac{\partial s^{\mathrm{g}}}{\partial \epsilon^{\mathrm{g}}} = s^{\mathrm{g}} - \rho^{\mathrm{g}} \frac{\partial s^{\mathrm{g}}}{\partial \rho^{\mathrm{g}}} - \epsilon^{\mathrm{g}} \frac{\partial s^{\mathrm{g}}}{\partial \epsilon^{\mathrm{g}}}. \tag{13}$$

For our later analysis, it is useful to rewrite the antisymmetric Poisson bracket (12) by means of some integrations by parts in the form,

$$\begin{aligned}
\{A,B\}^{\mathrm{g}} = &- \int_{V^{\mathrm{g}}} \frac{\partial a^{\mathrm{g}}}{\partial \rho^{\mathrm{g}}} \frac{\partial}{\partial \boldsymbol{r}} \cdot \left(\frac{\partial b^{\mathrm{g}}}{\partial \boldsymbol{M}^{\mathrm{g}}} \rho^{\mathrm{g}} \right) d^3r \\
&- \int_{V^{\mathrm{g}}} \frac{\partial a^{\mathrm{g}}}{\partial \boldsymbol{M}^{\mathrm{g}}} \frac{\partial}{\partial \boldsymbol{r}} : \left[\frac{\partial b^{\mathrm{g}}}{\partial \boldsymbol{M}^{\mathrm{g}}} \boldsymbol{M}^{\mathrm{g}} + (\tilde{b}^{\mathrm{g}} - b^{\mathrm{g}}) \boldsymbol{1} \right] d^3r \\
&- \int_{V^{\mathrm{g}}} \frac{\partial a^{\mathrm{g}}}{\partial \epsilon^{\mathrm{g}}} \left[\frac{\partial}{\partial \boldsymbol{r}} \cdot \left(\frac{\partial b^{\mathrm{g}}}{\partial \boldsymbol{M}^{\mathrm{g}}} \epsilon^{\mathrm{g}} \right) + p^{\mathrm{g}} \frac{\partial}{\partial \boldsymbol{r}} \cdot \frac{\partial b^{\mathrm{g}}}{\partial \boldsymbol{M}^{\mathrm{g}}} \right] d^3r \\
&+ \int_I \tilde{a}^{\mathrm{g}} \frac{\partial b^{\mathrm{g}}}{\partial \boldsymbol{M}^{\mathrm{g}}} \cdot \boldsymbol{n} \, d^2r,
\end{aligned} \tag{14}$$

where the normal unit vector $\boldsymbol{n}$ points from V^{g} into V^{l} and, for any observable A with density a^{g} in the gas,

$$\tilde{a}^{\mathrm{g}}(\rho^{\mathrm{g}}, \boldsymbol{M}^{\mathrm{g}}, \epsilon^{\mathrm{g}}) = \left[\rho^{\mathrm{g}} \frac{\partial}{\partial \rho^{\mathrm{g}}} + \boldsymbol{M}^{\mathrm{g}} \cdot \frac{\partial}{\partial \boldsymbol{M}^{\mathrm{g}}} + (\epsilon^{\mathrm{g}} + p^{\mathrm{g}}) \frac{\partial}{\partial \epsilon^{\mathrm{g}}} \right] a^{\mathrm{g}}(\rho^{\mathrm{g}}, \boldsymbol{M}^{\mathrm{g}}, \epsilon^{\mathrm{g}}). \tag{15}$$

Among the usual densities, only $\tilde{\epsilon}^{\mathrm{g}}$ differs from ϵ^{g} (see Table I). Note that $\tilde{\epsilon}^{\mathrm{g}} = \epsilon^{\mathrm{g}} + p^{\mathrm{g}}$ is the enthalpy density.

In the liquid phase, we similarly have

$$
\begin{aligned}
\{A,B\}^{\mathrm{l}} = & -\int_{V^{\mathrm{l}}} \rho^{\mathrm{l}}\left(\frac{\partial a^{\mathrm{l}}}{\partial \boldsymbol{M}^{\mathrm{l}}}\cdot\frac{\partial}{\partial \boldsymbol{r}}\frac{\partial b^{\mathrm{l}}}{\partial \rho^{\mathrm{l}}} - \frac{\partial b^{\mathrm{l}}}{\partial \boldsymbol{M}^{\mathrm{l}}}\cdot\frac{\partial}{\partial \boldsymbol{r}}\frac{\partial a^{\mathrm{l}}}{\partial \rho^{\mathrm{l}}}\right)d^3r \\
& -\int_{V^{\mathrm{l}}} \boldsymbol{M}^{\mathrm{l}}\cdot\left(\frac{\partial a^{\mathrm{l}}}{\partial \boldsymbol{M}^{\mathrm{l}}}\cdot\frac{\partial}{\partial \boldsymbol{r}}\frac{\partial b^{\mathrm{l}}}{\partial \boldsymbol{M}^{\mathrm{l}}} - \frac{\partial b^{\mathrm{l}}}{\partial \boldsymbol{M}^{\mathrm{l}}}\cdot\frac{\partial}{\partial \boldsymbol{r}}\frac{\partial a^{\mathrm{l}}}{\partial \boldsymbol{M}^{\mathrm{l}}}\right)d^3r \\
& -\int_{V^{\mathrm{l}}} \epsilon^{\mathrm{l}}\left(\frac{\partial a^{\mathrm{l}}}{\partial \boldsymbol{M}^{\mathrm{l}}}\cdot\frac{\partial}{\partial \boldsymbol{r}}\frac{\partial b^{\mathrm{l}}}{\partial \epsilon^{\mathrm{l}}} - \frac{\partial b^{\mathrm{l}}}{\partial \boldsymbol{M}^{\mathrm{l}}}\cdot\frac{\partial}{\partial \boldsymbol{r}}\frac{\partial a^{\mathrm{l}}}{\partial \epsilon^{\mathrm{l}}}\right)d^3r \\
& -\int_{V^{\mathrm{l}}} \left[\frac{\partial a^{\mathrm{l}}}{\partial \boldsymbol{M}^{\mathrm{l}}}\cdot\frac{\partial}{\partial \boldsymbol{r}}\left(p^{\mathrm{l}}\frac{\partial b^{\mathrm{l}}}{\partial \epsilon^{\mathrm{l}}}\right) - \frac{\partial b^{\mathrm{l}}}{\partial \boldsymbol{M}^{\mathrm{l}}}\cdot\frac{\partial}{\partial \boldsymbol{r}}\left(p^{\mathrm{l}}\frac{\partial a^{\mathrm{l}}}{\partial \epsilon^{\mathrm{l}}}\right)\right]d^3r \\
& +\int_{V^{\mathrm{l}}} \frac{\partial c^{\mathrm{l}}}{\partial \boldsymbol{r}}\cdot\left(\frac{\partial a^{\mathrm{l}}}{\partial \boldsymbol{M}^{\mathrm{l}}}\frac{\partial b^{\mathrm{l}}}{\partial c^{\mathrm{l}}} - \frac{\partial b^{\mathrm{l}}}{\partial \boldsymbol{M}^{\mathrm{l}}}\frac{\partial a^{\mathrm{l}}}{\partial c^{\mathrm{l}}}\right)d^3r, \qquad (16)
\end{aligned}
$$

where p^{l} is the pressure in the liquid given by

$$
p^{\mathrm{l}}\frac{\partial s^{\mathrm{l}}}{\partial \epsilon^{\mathrm{l}}} = s^{\mathrm{l}} - \rho^{\mathrm{l}}\frac{\partial s^{\mathrm{l}}}{\partial \rho^{\mathrm{l}}} - \epsilon^{\mathrm{l}}\frac{\partial s^{\mathrm{l}}}{\partial \epsilon^{\mathrm{l}}}. \qquad (17)
$$

Again, we offer a useful reformulation,

$$
\begin{aligned}
\{A,B\}^{\mathrm{l}} = & -\int_{V^{\mathrm{l}}} \frac{\partial a^{\mathrm{l}}}{\partial \rho^{\mathrm{l}}}\frac{\partial}{\partial \boldsymbol{r}}\cdot\left(\frac{\partial b^{\mathrm{l}}}{\partial \boldsymbol{M}^{\mathrm{l}}}\rho^{\mathrm{l}}\right)d^3r \\
& -\int_{V^{\mathrm{l}}} \frac{\partial a^{\mathrm{l}}}{\partial \boldsymbol{M}^{\mathrm{l}}}\frac{\partial}{\partial \boldsymbol{r}}:\left[\frac{\partial b^{\mathrm{l}}}{\partial \boldsymbol{M}^{\mathrm{l}}}\boldsymbol{M}^{\mathrm{l}} + (\tilde{b}^{\mathrm{l}} - b^{\mathrm{l}})\boldsymbol{1}\right]d^3r \\
& -\int_{V^{\mathrm{l}}} \frac{\partial a^{\mathrm{l}}}{\partial \epsilon^{\mathrm{l}}}\left[\frac{\partial}{\partial \boldsymbol{r}}\cdot\left(\frac{\partial b^{\mathrm{l}}}{\partial \boldsymbol{M}^{\mathrm{l}}}\epsilon^{\mathrm{l}}\right) + p^{\mathrm{l}}\frac{\partial}{\partial \boldsymbol{r}}\cdot\frac{\partial b^{\mathrm{l}}}{\partial \boldsymbol{M}^{\mathrm{l}}}\right]d^3r \\
& -\int_{V^{\mathrm{l}}} \frac{\partial a^{\mathrm{l}}}{\partial c^{\mathrm{l}}}\frac{\partial b^{\mathrm{l}}}{\partial \boldsymbol{M}^{\mathrm{l}}}\cdot\frac{\partial c^{\mathrm{l}}}{\partial \boldsymbol{r}}d^3r - \int_I \tilde{a}^{\mathrm{l}}\frac{\partial b^{\mathrm{l}}}{\partial \boldsymbol{M}^{\mathrm{l}}}\cdot\boldsymbol{n}\,d^2r, \qquad (18)
\end{aligned}
$$

where the normal unit vector $\boldsymbol{n}$ at the gas-liquid interface points into V^{l} and, for any observable A with density a^{l} in the liquid,

$$
\begin{aligned}
\tilde{a}^{\mathrm{l}}(\rho^{\mathrm{l}},\boldsymbol{M}^{\mathrm{l}},\epsilon^{\mathrm{l}},c^{\mathrm{l}}) = & \left[\rho^{\mathrm{l}}\frac{\partial}{\partial \rho^{\mathrm{l}}} + \boldsymbol{M}^{\mathrm{l}}\cdot\frac{\partial}{\partial \boldsymbol{M}^{\mathrm{l}}}\right. \\
& \left. + (\epsilon^{\mathrm{l}} + p^{\mathrm{l}})\frac{\partial}{\partial \epsilon^{\mathrm{l}}}\right]a^{\mathrm{l}}(\rho^{\mathrm{l}},\boldsymbol{M}^{\mathrm{l}},\epsilon^{\mathrm{l}},c^{\mathrm{l}}). \qquad (19)
\end{aligned}
$$

Finally, the interfacial contribution to the Poisson bracket is

$$
\begin{aligned}
\{A,B\}^{\mathrm{s}} = & -\int_I \rho^{\mathrm{s}}\left(\frac{\partial a^{\mathrm{s}}}{\partial \boldsymbol{M}^{\mathrm{s}}}\cdot\frac{\partial}{\partial \boldsymbol{r}_\parallel}\frac{\partial b^{\mathrm{s}}}{\partial \rho^{\mathrm{s}}} - \frac{\partial b^{\mathrm{s}}}{\partial \boldsymbol{M}^{\mathrm{s}}}\cdot\frac{\partial}{\partial \boldsymbol{r}_\parallel}\frac{\partial a^{\mathrm{s}}}{\partial \rho^{\mathrm{s}}}\right)d^2r \\
& -\int_I \boldsymbol{M}^{\mathrm{s}}\cdot\left(\frac{\partial a^{\mathrm{s}}}{\partial \boldsymbol{M}^{\mathrm{s}}}\cdot\frac{\partial}{\partial \boldsymbol{r}_\parallel}\frac{\partial b^{\mathrm{s}}}{\partial \boldsymbol{M}^{\mathrm{s}}} - \frac{\partial b^{\mathrm{s}}}{\partial \boldsymbol{M}^{\mathrm{s}}}\cdot\frac{\partial}{\partial \boldsymbol{r}_\parallel}\frac{\partial a^{\mathrm{s}}}{\partial \boldsymbol{M}^{\mathrm{s}}}\right)d^2r \\
& -\int_I \epsilon^{\mathrm{s}}\left(\frac{\partial a^{\mathrm{s}}}{\partial \boldsymbol{M}^{\mathrm{s}}}\cdot\frac{\partial}{\partial \boldsymbol{r}_\parallel}\frac{\partial b^{\mathrm{s}}}{\partial \epsilon^{\mathrm{s}}} - \frac{\partial b^{\mathrm{s}}}{\partial \boldsymbol{M}^{\mathrm{s}}}\cdot\frac{\partial}{\partial \boldsymbol{r}_\parallel}\frac{\partial a^{\mathrm{s}}}{\partial \epsilon^{\mathrm{s}}}\right)d^2r \\
& -\int_I \left[\frac{\partial a^{\mathrm{s}}}{\partial \boldsymbol{M}^{\mathrm{s}}}\cdot\frac{\partial}{\partial \boldsymbol{r}_\parallel}\left(p^{\mathrm{s}}\frac{\partial b^{\mathrm{s}}}{\partial \epsilon^{\mathrm{s}}}\right) - \frac{\partial b^{\mathrm{s}}}{\partial \boldsymbol{M}^{\mathrm{s}}}\cdot\frac{\partial}{\partial \boldsymbol{r}_\parallel}\left(p^{\mathrm{s}}\frac{\partial a^{\mathrm{s}}}{\partial \epsilon^{\mathrm{s}}}\right)\right]d^2r \\
& +\int_I \frac{\partial c^{\mathrm{l}}}{\partial \boldsymbol{r}_\parallel}\cdot\left(\frac{\partial a^{\mathrm{s}}}{\partial \boldsymbol{M}^{\mathrm{s}}}\frac{\partial b^{\mathrm{s}}}{\partial c^{\mathrm{l}}} - \frac{\partial b^{\mathrm{s}}}{\partial \boldsymbol{M}^{\mathrm{s}}}\frac{\partial a^{\mathrm{s}}}{\partial c^{\mathrm{l}}}\right)d^2r, \qquad (20)
\end{aligned}
$$

where spatial derivatives of interfacial variables can only be formed within the interface. In formulating the last term in Eq. (20), we have assumed that the interfacial contribution to an observable can depend only on intensive bulk variables, such as c^{l}, and we simply convect such a variable when occurring in a^{s}, b^{s} with the interfacial velocity (this term is necessary to guarantee the degeneracy of the entropy in our simple treatment of the condition $c^{\mathrm{s}}=c^{\mathrm{l}}$). The surface pressure is given by

$$
p^{\mathrm{s}}\frac{\partial s^{\mathrm{s}}}{\partial \epsilon^{\mathrm{s}}} = s^{\mathrm{s}} - \epsilon^{\mathrm{s}}\frac{\partial s^{\mathrm{s}}}{\partial \epsilon^{\mathrm{s}}} \quad \text{or} \quad -p^{\mathrm{s}} = \epsilon^{\mathrm{s}} - T^{\mathrm{s}}s^{\mathrm{s}}. \qquad (21)
$$

The function $s^{\mathrm{s}}(\epsilon^{\mathrm{s}})$ thus encodes all information about what is known as the interfacial tension $-p^{\mathrm{s}}$, including the functional dependence on the thermodynamic variable characterizing the interface. The intensive composition variable does not contribute to the pressure in the above equations. The expression (20) can be rewritten in the more compact form,

$$
\{A,B\}^{\mathrm{s}} = -\int_I \left[\frac{\partial a^{\mathrm{s}}}{\partial \boldsymbol{M}^{\mathrm{s}}}\cdot\frac{\partial}{\partial \boldsymbol{r}_\parallel}(\tilde{b}^{\mathrm{s}} - b^{\mathrm{s}}) - \frac{\partial b^{\mathrm{s}}}{\partial \boldsymbol{M}^{\mathrm{s}}}\cdot\frac{\partial}{\partial \boldsymbol{r}_\parallel}(\tilde{a}^{\mathrm{s}} - a^{\mathrm{s}})\right]d^2r, \qquad (22)
$$

in terms of

$$
\begin{aligned}
\tilde{a}^{\mathrm{s}}(\rho^{\mathrm{s}},\boldsymbol{M}^{\mathrm{s}},\epsilon^{\mathrm{s}}) = & \left[\rho^{\mathrm{s}}\frac{\partial}{\partial \rho^{\mathrm{s}}} + \boldsymbol{M}^{\mathrm{s}}\cdot\frac{\partial}{\partial \boldsymbol{M}^{\mathrm{s}}}\right. \\
& \left. + (\epsilon^{\mathrm{s}} + p^{\mathrm{s}})\frac{\partial}{\partial \epsilon^{\mathrm{s}}}\right]a^{\mathrm{s}}(\rho^{\mathrm{s}},\boldsymbol{M}^{\mathrm{s}},\epsilon^{\mathrm{s}}). \qquad (23)
\end{aligned}
$$

For later convenience, we perform an integration by parts in Eq. (22) and neglect one-dimensional boundary terms to obtain

$$
\begin{aligned}
\{A,B\}^{\mathrm{s}} = & -\int_I \left[\frac{\partial a^{\mathrm{s}}}{\partial \boldsymbol{M}^{\mathrm{s}}}\cdot\frac{\partial}{\partial \boldsymbol{r}_\parallel}(\tilde{b}^{\mathrm{s}} - b^{\mathrm{s}}) + \tilde{a}^{\mathrm{s}}\frac{\partial}{\partial \boldsymbol{r}_\parallel}\cdot\frac{\partial b^{\mathrm{s}}}{\partial \boldsymbol{M}^{\mathrm{s}}_\parallel}\right. \\
& \left. + \frac{\partial b^{\mathrm{s}}}{\partial \boldsymbol{M}^{\mathrm{s}}}\cdot\frac{\partial}{\partial \boldsymbol{r}_\parallel}a^{\mathrm{s}}\right]d^2r. \qquad (24)
\end{aligned}
$$

To integrate by parts in the interface, we have used the auxiliary formula

$$
\begin{aligned}
\int_I \boldsymbol{f}\cdot\frac{\partial}{\partial \boldsymbol{r}_\parallel}g\,d^2r & = -\int_I g\frac{\partial}{\partial \boldsymbol{r}_\parallel}\cdot\boldsymbol{f}\,d^2r + \int_I g\boldsymbol{f}\cdot\boldsymbol{n}\frac{\partial}{\partial \boldsymbol{r}_\parallel}\cdot\boldsymbol{n}\,d^2r \\
& = -\int_I g\frac{\partial}{\partial \boldsymbol{r}_\parallel}\cdot\boldsymbol{f}_\parallel d^2r, \qquad (25)
\end{aligned}
$$

where $\boldsymbol{f}_\parallel=(\boldsymbol{1}-\boldsymbol{n}\boldsymbol{n})\cdot\boldsymbol{f}$.

To obtain consistency between the fundamental thermodynamic evolution equation and the chain rule of functional calculus, we finally introduce a further interfacial bracket contribution, which we refer to as the moving interface normal transfer (MINT) term,

$$\{A,B\}^{\mathrm{mint}} = \int_I \frac{\partial a^{\mathrm{s}}}{\partial \boldsymbol{M}^{\mathrm{s}}} \cdot \boldsymbol{n} \left[(\tilde{b}^{\mathrm{g}} - b^{\mathrm{g}}) - (\tilde{b}^{\mathrm{l}} - b^{\mathrm{l}}) + (\tilde{b}^{\mathrm{s}} - b^{\mathrm{s}}) \frac{\partial}{\partial \boldsymbol{r}_{\parallel}} \cdot \boldsymbol{n} \right] d^2 r - \int_I \frac{\partial b^{\mathrm{s}}}{\partial \boldsymbol{M}^{\mathrm{s}}} \cdot \boldsymbol{n} \left[(\tilde{a}^{\mathrm{g}} - a^{\mathrm{g}}) - (\tilde{a}^{\mathrm{l}} - a^{\mathrm{l}}) + (\tilde{a}^{\mathrm{s}} - a^{\mathrm{s}}) \frac{\partial}{\partial \boldsymbol{r}_{\parallel}} \cdot \boldsymbol{n} \right] d^2 r. \tag{26}$$

This antisymmetric term is not of the proper form for a Poisson bracket because it is not even a derivation (the observables appear not only through derivatives). In the presence of moving interfaces, however, the structure of the chain rule is incompatible with the Poisson bracket structure (see below), so that the introduction of a MINT is actually unavoidable.

With the above definitions of brackets, we find the following degeneracy properties for the entropy (7) and for the total and species masses introduced in Eqs. (9) and (10):

$$\{M^{\mathrm{tot}},B\} = 0, \quad \{M^{\mathrm{tot}},B\}^{\mathrm{mint}} = 0, \tag{27}$$

$$\{M^{\mathrm{g/s}},B\} = 0, \quad \{M^{\mathrm{g/s}},B\}^{\mathrm{mint}} = 0, \tag{28}$$

$$\{S,B\} = 0, \quad \{S,B\}^{\mathrm{mint}} = 0. \tag{29}$$

If $\mathcal{M}$ is the total momentum, we obtain

$$-\{\mathcal{M},B\} = \{\mathcal{M},B\}^{\mathrm{mint}} = \int_I \boldsymbol{n} \left[(\tilde{b}^{\mathrm{g}} - b^{\mathrm{g}}) - (\tilde{b}^{\mathrm{l}} - b^{\mathrm{l}}) + (\tilde{b}^{\mathrm{s}} - b^{\mathrm{s}}) \frac{\partial}{\partial \boldsymbol{r}_{\parallel}} \cdot \boldsymbol{n} \right] d^2 r, \tag{30}$$

which shows that the MINT is crucial to guarantee momentum conservation in the form of the degeneracy condition,

$$\{\mathcal{M},B\} + \{\mathcal{M},B\}^{\mathrm{mint}} = 0. \tag{31}$$

The most important reason for introducing the MINT is to obtain structural consistency with the chain rule, as shown below.

E. Dissipative bracket

We express the dissipative bracket as a sum of bulk and interface contributions,

$$[A,B] = [A,B]^{\mathrm{g}} + [A,B]^{\mathrm{l}} + [A,B]^{\mathrm{s}}. \tag{32}$$

In the gas phase, we have the usual dissipative processes associated with flow and heat conduction [8,29],

$$[A,B]^{\mathrm{g}} = \int_{V^{\mathrm{g}}} 2\eta^{\mathrm{g}} T^{\mathrm{g}} \left(\widehat{\frac{\partial}{\partial \boldsymbol{r}} \frac{\partial a^{\mathrm{g}}}{\partial \boldsymbol{M}^{\mathrm{g}}}} - \hat{\boldsymbol{\kappa}}^{\mathrm{g}} \frac{\partial a^{\mathrm{g}}}{\partial \epsilon^{\mathrm{g}}} \right) : \left(\widehat{\frac{\partial}{\partial \boldsymbol{r}} \frac{\partial b^{\mathrm{g}}}{\partial \boldsymbol{M}^{\mathrm{g}}}} - \hat{\boldsymbol{\kappa}}^{\mathrm{g}} \frac{\partial b^{\mathrm{g}}}{\partial \epsilon^{\mathrm{g}}} \right) d^3 r + \int_{V^{\mathrm{g}}} \kappa^{\mathrm{g}} T^{\mathrm{g}} \left(\frac{\partial}{\partial \boldsymbol{r}} \cdot \frac{\partial a^{\mathrm{g}}}{\partial \boldsymbol{M}^{\mathrm{g}}} - \mathrm{tr}\, \boldsymbol{\kappa}^{\mathrm{g}} \frac{\partial a^{\mathrm{g}}}{\partial \epsilon^{\mathrm{g}}} \right) \times \left(\frac{\partial}{\partial \boldsymbol{r}} \cdot \frac{\partial b^{\mathrm{g}}}{\partial \boldsymbol{M}^{\mathrm{g}}} - \mathrm{tr}\, \boldsymbol{\kappa}^{\mathrm{g}} \frac{\partial b^{\mathrm{g}}}{\partial \epsilon^{\mathrm{g}}} \right) d^3 r + \int_{V^{\mathrm{g}}} \lambda^{\mathrm{g}} {T^{\mathrm{g}}}^2 \left(\frac{\partial}{\partial \boldsymbol{r}} \frac{\partial a^{\mathrm{g}}}{\partial \epsilon^{\mathrm{g}}} \right) \cdot \left(\frac{\partial}{\partial \boldsymbol{r}} \frac{\partial b^{\mathrm{g}}}{\partial \epsilon^{\mathrm{g}}} \right) d^3 r, \tag{33}$$

where η^{g} is the viscosity, κ^{g} is the bulk viscosity, λ^{g} is the thermal conductivity, and $\boldsymbol{\kappa}^{\mathrm{g}}$ is the velocity gradient tensor in the gas phase. The wide hat over a tensor indicates the symmetrized traceless part of that tensor.

In the two-component liquid, we have diffusion in addition to the usual dissipative processes associated with flow and heat conduction,

$$[A,B]^{\mathrm{l}} = \int_{V^{\mathrm{l}}} 2\eta^{\mathrm{l}} T^{\mathrm{l}} \left(\widehat{\frac{\partial}{\partial \boldsymbol{r}} \frac{\partial a^{\mathrm{l}}}{\partial \boldsymbol{M}^{\mathrm{l}}}} - \hat{\boldsymbol{\kappa}}^{\mathrm{l}} \frac{\partial a^{\mathrm{l}}}{\partial \epsilon^{\mathrm{l}}} \right) : \left(\widehat{\frac{\partial}{\partial \boldsymbol{r}} \frac{\partial b^{\mathrm{l}}}{\partial \boldsymbol{M}^{\mathrm{l}}}} - \hat{\boldsymbol{\kappa}}^{\mathrm{l}} \frac{\partial b^{\mathrm{l}}}{\partial \epsilon^{\mathrm{l}}} \right) d^3 r + \int_{V^{\mathrm{l}}} \kappa^{\mathrm{l}} T^{\mathrm{l}} \left(\frac{\partial}{\partial \boldsymbol{r}} \cdot \frac{\partial a^{\mathrm{l}}}{\partial \boldsymbol{M}^{\mathrm{l}}} - \mathrm{tr}\, \boldsymbol{\kappa}^{\mathrm{l}} \frac{\partial a^{\mathrm{l}}}{\partial \epsilon^{\mathrm{l}}} \right) \left(\frac{\partial}{\partial \boldsymbol{r}} \cdot \frac{\partial b^{\mathrm{l}}}{\partial \boldsymbol{M}^{\mathrm{l}}} - \mathrm{tr}\, \boldsymbol{\kappa}^{\mathrm{l}} \frac{\partial b^{\mathrm{l}}}{\partial \epsilon^{\mathrm{l}}} \right) d^3 r + \int_{V^{\mathrm{l}}} \lambda^{\mathrm{l}} {T^{\mathrm{l}}}^2 \left(\frac{\partial}{\partial \boldsymbol{r}} \frac{\partial a^{\mathrm{l}}}{\partial \epsilon^{\mathrm{l}}} \right) \cdot \left(\frac{\partial}{\partial \boldsymbol{r}} \frac{\partial b^{\mathrm{l}}}{\partial \epsilon^{\mathrm{l}}} \right) d^3 r + \int_{V^{\mathrm{l}}} \tilde{D}^{\mathrm{l}} \left[\frac{\partial}{\partial \boldsymbol{r}} \left(\frac{1}{\rho^{\mathrm{l}}} \frac{\partial a^{\mathrm{l}}}{\partial c^{\mathrm{l}}} \right) \right] \cdot \left[\frac{\partial}{\partial \boldsymbol{r}} \left(\frac{1}{\rho^{\mathrm{l}}} \frac{\partial b^{\mathrm{l}}}{\partial c^{\mathrm{l}}} \right) \right] d^3 r, \tag{34}$$

where $\tilde{D}^{\mathrm{l}}$ is related to the diffusion coefficient. Up to this point of the development, not much thinking was required. All the thermodynamic building blocks are based entirely on the previous experience with hydrodynamics.

For the interfacial contribution to the dissipative bracket, we postulate

$$[A,B]^{\mathrm{s}} = \int_I \frac{T^{\mathrm{g}} T^{\mathrm{s}}}{R_{\mathrm{K}}^{\mathrm{gs}}} \left(\frac{\partial a^{\mathrm{g}}}{\partial \epsilon^{\mathrm{g}}} - \frac{\partial a^{\mathrm{s}}}{\partial \epsilon^{\mathrm{s}}} \right) \left(\frac{\partial b^{\mathrm{g}}}{\partial \epsilon^{\mathrm{g}}} - \frac{\partial b^{\mathrm{s}}}{\partial \epsilon^{\mathrm{s}}} \right) d^2 r + \int_I \frac{T^{\mathrm{l}} T^{\mathrm{s}}}{R_{\mathrm{K}}^{\mathrm{ls}}} \left(\frac{\partial a^{\mathrm{l}}}{\partial \epsilon^{\mathrm{l}}} - \frac{\partial a^{\mathrm{s}}}{\partial \epsilon^{\mathrm{s}}} \right) \left(\frac{\partial b^{\mathrm{l}}}{\partial \epsilon^{\mathrm{l}}} - \frac{\partial b^{\mathrm{s}}}{\partial \epsilon^{\mathrm{s}}} \right) d^2 r + \int_I \left(\frac{\partial a^{\mathrm{g}}}{\partial \boldsymbol{M}^{\mathrm{g}}} - \frac{\partial a^{\mathrm{s}}}{\partial \boldsymbol{M}^{\mathrm{s}}} - \boldsymbol{v}^{\mathrm{g}} \frac{\partial a^{\mathrm{g}}}{\partial \epsilon^{\mathrm{g}}} + \boldsymbol{v}^{\mathrm{s}} \frac{\partial a^{\mathrm{s}}}{\partial \epsilon^{\mathrm{s}}} \right) \cdot T^{\mathrm{s}} \boldsymbol{\zeta}^{\mathrm{gs}} \cdot \left(\frac{\partial b^{\mathrm{g}}}{\partial \boldsymbol{M}^{\mathrm{g}}} - \frac{\partial b^{\mathrm{s}}}{\partial \boldsymbol{M}^{\mathrm{s}}} - \boldsymbol{v}^{\mathrm{g}} \frac{\partial b^{\mathrm{g}}}{\partial \epsilon^{\mathrm{g}}} + \boldsymbol{v}^{\mathrm{s}} \frac{\partial b^{\mathrm{s}}}{\partial \epsilon^{\mathrm{s}}} \right) d^2 r + \int_I \left(\frac{\partial a^{\mathrm{l}}}{\partial \boldsymbol{M}^{\mathrm{l}}} - \frac{\partial a^{\mathrm{s}}}{\partial \boldsymbol{M}^{\mathrm{s}}} - \boldsymbol{v}^{\mathrm{l}} \frac{\partial a^{\mathrm{l}}}{\partial \epsilon^{\mathrm{l}}} + \boldsymbol{v}^{\mathrm{s}} \frac{\partial a^{\mathrm{s}}}{\partial \epsilon^{\mathrm{s}}} \right) \cdot T^{\mathrm{s}} \boldsymbol{\zeta}^{\mathrm{ls}} \cdot \left(\frac{\partial b^{\mathrm{l}}}{\partial \boldsymbol{M}^{\mathrm{l}}} - \frac{\partial b^{\mathrm{s}}}{\partial \boldsymbol{M}^{\mathrm{s}}} - \boldsymbol{v}^{\mathrm{l}} \frac{\partial b^{\mathrm{l}}}{\partial \epsilon^{\mathrm{l}}} + \boldsymbol{v}^{\mathrm{s}} \frac{\partial b^{\mathrm{s}}}{\partial \epsilon^{\mathrm{s}}} \right) d^2 r + \int_I \Lambda \left\{ \frac{\partial a^{\mathrm{g}}}{\partial \rho^{\mathrm{g}}} - \frac{\partial a^{\mathrm{l}}}{\partial \rho^{\mathrm{l}}} - \frac{1 - c^{\mathrm{l}}}{\rho^{\mathrm{l}}} \frac{\partial a^{\mathrm{l}}}{\partial c^{\mathrm{l}}} + \frac{\boldsymbol{v}^{\mathrm{g}}}{2} \cdot \left[q^{\mathrm{g}} \boldsymbol{v}^{\mathrm{g}} \frac{\partial a^{\mathrm{g}}}{\partial \epsilon^{\mathrm{g}}} + (1 - q^{\mathrm{g}}) \frac{\partial a^{\mathrm{g}}}{\partial \boldsymbol{M}^{\mathrm{g}}} \right] - \frac{\boldsymbol{v}^{\mathrm{l}}}{2} \cdot \left[q^{\mathrm{l}} \boldsymbol{v}^{\mathrm{l}} \frac{\partial a^{\mathrm{l}}}{\partial \epsilon^{\mathrm{l}}} + (1 - q^{\mathrm{l}}) \frac{\partial a^{\mathrm{l}}}{\partial \boldsymbol{M}^{\mathrm{l}}} \right] \right\} \times \left\{ \frac{\partial b^{\mathrm{g}}}{\partial \rho^{\mathrm{g}}} - \frac{\partial b^{\mathrm{l}}}{\partial \rho^{\mathrm{l}}} - \frac{1 - c^{\mathrm{l}}}{\rho^{\mathrm{l}}} \frac{\partial b^{\mathrm{l}}}{\partial c^{\mathrm{l}}} + \frac{\boldsymbol{v}^{\mathrm{g}}}{2} \cdot \left[q^{\mathrm{g}} \boldsymbol{v}^{\mathrm{g}} \frac{\partial b^{\mathrm{g}}}{\partial \epsilon^{\mathrm{g}}} + (1 - q^{\mathrm{g}}) \frac{\partial b^{\mathrm{g}}}{\partial \boldsymbol{M}^{\mathrm{g}}} \right] - \frac{\boldsymbol{v}^{\mathrm{l}}}{2} \cdot \left[q^{\mathrm{l}} \boldsymbol{v}^{\mathrm{l}} \frac{\partial b^{\mathrm{l}}}{\partial \epsilon^{\mathrm{l}}} + (1 - q^{\mathrm{l}}) \frac{\partial b^{\mathrm{l}}}{\partial \boldsymbol{M}^{\mathrm{l}}} \right] \right\} d^2 r. \tag{35}$$

This dissipative bracket expresses the transfer of energy, momentum, and mass into and through the interface. The first integral in Eq. (35) describes the heat transfer between the gas and the interface in terms of the Kapitza resistance $R_{\mathrm{K}}^{\mathrm{gs}}$, which characterizes the thermal boundary resistance between a bulk fluid and a wall (or layer) [10,30]. The second integral represents an analogous heat transfer between the liquid and the interface in terms of the Kapitza resistance $R_{\mathrm{K}}^{\mathrm{ls}}$. The next two terms describe the potentially anisotropic momentum transfer between the different subsystems in terms of the friction tensors $\boldsymbol{\zeta}^{\mathrm{gs}}$ and $\boldsymbol{\zeta}^{\mathrm{ls}}$. The last integral in Eq. (35) describes the process by which solute from the supersaturated liquid is released into a growing gas bubble. The rate for this process is given by the coefficient Λ. In this dissipative contribution, the first three terms in each of the curly brackets express the basic exchange idea between solution and gas bubble and the further compensation terms are required to satisfy the conservation of energy. The parameters q^{g} and q^{l} allow a mixing of thermal and mechanical energy compensation. Species masses and energy are degenerate functionals for all contributions to the dissipative bracket. For the total momentum $\mathcal{M}$, we obtain

$$[\mathcal{M},S] = \int_I \frac{1}{2}[(1-q^{\mathrm{g}})\boldsymbol{v}^{\mathrm{g}} - (1-q^{\mathrm{l}})\boldsymbol{v}^{\mathrm{l}}]\Lambda\xi^{\mathrm{gl}} d^2r, \qquad (36)$$

which shows that only the choice $q^{\mathrm{g}}=q^{\mathrm{l}}=1$ in the dissipative bracket (35) leads to a degenerate total momentum. We hence assume $q^{\mathrm{g}}=q^{\mathrm{l}}=1$ from now on.

At this point, our thermodynamic modeling is complete. While the expressions for the generators and brackets look lengthy, one should realize that most of the terms merely express the well-known hydrodynamics of the bulk phases. The specific and new ideas to describe the processes at the interface are (i) the choice of the system variables, in particular, of the variables $x^{\mathrm{s}}=(\rho^{\mathrm{s}},\boldsymbol{M}^{\mathrm{s}},\epsilon^{\mathrm{s}})$, (ii) the obvious and most basic introduction of surface excess densities of energy (6) and entropy (7), and (iii) the formulation (35) of a dissipative bracket due to heat and momentum transfer between the bulk phases and the boundary layer and due to the release of solute from the boundary layer.

The remaining task is to extract and interpret all the time-evolution equations and boundary conditions from the thermodynamic building blocks.

F. Time-evolution equations and boundary conditions

According to the GENERIC framework [6–8], thermodynamically admissible evolution equations can be expressed in the format of the fundamental equation

$$\frac{dA}{dt} = \{A,E\} + [A,S]. \qquad (37)$$

In the presence of moving interfaces, for reasons of momentum conservation and structural consistency, we need to modify this fundamental equation into

$$\frac{dA}{dt} = \{A,E\} + \{A,E\}^{\mathrm{mint}} + [A,S]. \qquad (38)$$

The general strategy of nonequilibrium thermodynamics is to compare the definition of the functional derivatives, which has the appearance of a chain rule, to the bracket Eq. (38). For a functional A of the general form (1), the rate of change is given by the chain rule

$$\frac{dA}{dt} = \int_{V^{\mathrm{g}}} \frac{\partial a^{\mathrm{g}}}{\partial x^{\mathrm{g}}}\frac{\partial x^{\mathrm{g}}}{\partial t} d^3r + \int_{V^{\mathrm{l}}} \frac{\partial a^{\mathrm{l}}}{\partial x^{\mathrm{l}}}\frac{\partial x^{\mathrm{l}}}{\partial t} d^3r + \int_I \frac{\partial a^{\mathrm{s}}}{\partial t} d^2r + \int_I w_n^{\mathrm{s}}(a^{\mathrm{g}} - a^{\mathrm{l}}) d^2r + \int_I w_n^{\mathrm{s}} a^{\mathrm{s}} \frac{\partial}{\partial \boldsymbol{r}_{\parallel}} \cdot \boldsymbol{n} d^2r, \qquad (39)$$

where $w_n^{\mathrm{s}}=\boldsymbol{v}^{\mathrm{s}}\cdot\boldsymbol{n}$ is the normal velocity of the interface. A positive w_n^{s} implies that the liquid phase is replaced by the gas phase, as described by the first integral involving w_n^{s} in Eq. (39). The derivative $\partial a^{\mathrm{s}}/\partial t$ is not a conventional partial derivative because it cannot be evaluated at a fixed point in space. We need to follow the interface, and we do that in the direction normal to the interface. In that sense, this time derivative of an interfacial property is "as partial as possible;" flow effects within the interface are not taken into account by this derivative, there is just a minimal motion together with the interface. The last term in Eq. (39) is a further correction resulting from local changes of the interfacial area $w_n^{\mathrm{s}}\boldsymbol{\nabla}_{\parallel}\cdot\boldsymbol{n}$, where $\boldsymbol{n}$ is a normal unit vector pointing from V^{g} into V^{l}, just like there is a contribution to the partial time derivative of a bulk density deformed by a velocity field $\boldsymbol{v}$ due to changes of volume $\boldsymbol{\nabla}\cdot\boldsymbol{v}$ (note that $-\boldsymbol{\nabla}_{\parallel}\cdot\boldsymbol{n}$ is the mean curvature of the interface [3], for example, $\boldsymbol{\nabla}_{\parallel}\cdot\boldsymbol{n}=2/R$ for a sphere of radius R; smaller radius or larger curvature implies a larger rate of change under normal motion).

The chain rule (39) may actually be considered as a definition of the functional derivative of A in the presence of a moving interface; but only partial derivatives of the densities a^{g}, a^{l}, and a^{s} occur because the functional depends only on x^{g}, x^{l}, and x^{s} as shown in Eq. (1). The more general case of functionals depending also on spatial derivatives of the independent variables has been discussed with mathematical rigor in [31].

The last two integrals in Eq. (39) are related to the normal motion of interfaces. They involve the densities a^{g}, a^{l}, and a^{s} themselves rather than only their derivatives. Their presence in the chain rule is the reason why we need to introduce a corresponding MINT in Eq. (38). Note that there is a close formal resemblance of the last two integrals and the structure of the MINT (26). Further note that the correction terms due to the motion of the interface in Eq. (39) are intimately related to the gauge transformation (2), so that we can easily incorporate curvature effects into the latter,

$$a^{\mathrm{s}} \to a^{\mathrm{s}} + \ell\left(a^{\mathrm{g}} - a^{\mathrm{l}} + a^{\mathrm{s}}\frac{\partial}{\partial \boldsymbol{r}_{\parallel}}\cdot\boldsymbol{n}\right). \qquad (40)$$

For gauge transformations, however, the curvature corrections are expected to be unimportant because a^{s} is either gauge invariant or small.

The expected bulk equations are obtained as in the absence of interfaces. We do not list these well-known hydrodynamic equations (except for the special case of spherical symmetry discussed in detail below). The more interesting evolution equation for any interfacial density a^{s} becomes

$$\begin{aligned}
&\frac{\partial a^{\mathrm{s}}}{\partial t}+\tilde{a}^{\mathrm{s}}\frac{\partial}{\partial \boldsymbol{r}_{\parallel}}\cdot\boldsymbol{v}_{\parallel}^{\mathrm{s}}+\boldsymbol{v}_{\parallel}^{\mathrm{s}}\cdot\frac{\partial}{\partial \boldsymbol{r}_{\parallel}}a^{\mathrm{s}}+w_n^{\mathrm{s}}\tilde{a}^{\mathrm{s}}\frac{\partial}{\partial \boldsymbol{r}_{\parallel}}\cdot\boldsymbol{n}\\
&=[\tilde{a}^{\mathrm{g}}(\boldsymbol{v}^{\mathrm{g}}-\boldsymbol{v}^{\mathrm{s}})-\tilde{a}^{\mathrm{l}}(\boldsymbol{v}^{\mathrm{l}}-\boldsymbol{v}^{\mathrm{s}})]\cdot\boldsymbol{n}+\left(\frac{\partial a^{\mathrm{g}}}{\partial\rho^{\mathrm{g}}}-\frac{\partial a^{\mathrm{l}}}{\partial\rho^{\mathrm{l}}}\right)\Lambda\xi^{\mathrm{gl}}-\frac{1}{\rho^{\mathrm{l}}}\frac{\partial a^{\mathrm{l}}}{\partial c^{\mathrm{l}}}\left[(1-c^{\mathrm{l}})\Lambda\xi^{\mathrm{gl}}+\tilde{D}^{\mathrm{l}}\boldsymbol{n}\cdot\frac{\partial}{\partial\boldsymbol{r}}\left(\frac{1}{\rho^{\mathrm{l}}}\frac{\partial s^{\mathrm{l}}(\rho^{\mathrm{l}},\epsilon^{\mathrm{l}},c^{\mathrm{l}})}{\partial c^{\mathrm{l}}}\right)\right]\\
&\quad-\frac{\partial a^{\mathrm{s}}}{\partial\boldsymbol{M}^{\mathrm{s}}}\cdot\frac{\partial p^{\mathrm{s}}}{\partial\boldsymbol{r}_{\parallel}}+\frac{\partial a^{\mathrm{s}}}{\partial\boldsymbol{M}^{\mathrm{s}}}\cdot\boldsymbol{n}\left(p^{\mathrm{g}}-p^{\mathrm{l}}+p^{\mathrm{s}}\frac{\partial}{\partial\boldsymbol{r}_{\parallel}}\cdot\boldsymbol{n}\right)-\left(\frac{\partial a^{\mathrm{g}}}{\partial\boldsymbol{M}^{\mathrm{g}}}-\frac{\partial a^{\mathrm{s}}}{\partial\boldsymbol{M}^{\mathrm{s}}}\right)\cdot\boldsymbol{\zeta}^{\mathrm{gs}}\cdot\left(\frac{T^{\mathrm{s}}}{T^{\mathrm{g}}}\boldsymbol{v}^{\mathrm{g}}-\boldsymbol{v}^{\mathrm{s}}\right)-\left(\frac{\partial a^{\mathrm{l}}}{\partial\boldsymbol{M}^{\mathrm{l}}}-\frac{\partial a^{\mathrm{s}}}{\partial\boldsymbol{M}^{\mathrm{s}}}\right)\\
&\quad\cdot\boldsymbol{\zeta}^{\mathrm{ls}}\cdot\left(\frac{T^{\mathrm{s}}}{T^{\mathrm{l}}}\boldsymbol{v}^{\mathrm{l}}-\boldsymbol{v}^{\mathrm{s}}\right)-\frac{\partial a^{\mathrm{g}}}{\partial\boldsymbol{M}^{\mathrm{g}}}\cdot(2\eta^{\mathrm{g}}\hat{\boldsymbol{\kappa}}^{\mathrm{g}}+\kappa^{\mathrm{g}}\operatorname{tr}\boldsymbol{\kappa}^{\mathrm{g}}\mathbf{1})\cdot\boldsymbol{n}+\frac{\partial a^{\mathrm{l}}}{\partial\boldsymbol{M}^{\mathrm{l}}}\cdot(2\eta^{\mathrm{l}}\hat{\boldsymbol{\kappa}}^{\mathrm{l}}+\kappa^{\mathrm{l}}\operatorname{tr}\boldsymbol{\kappa}^{\mathrm{l}}\mathbf{1})\cdot\boldsymbol{n}+\left(\frac{\partial a^{\mathrm{g}}}{\partial\epsilon^{\mathrm{g}}}\boldsymbol{v}^{\mathrm{g}}-\frac{\partial a^{\mathrm{s}}}{\partial\epsilon^{\mathrm{s}}}\boldsymbol{v}^{\mathrm{s}}\right)\\
&\quad\cdot\boldsymbol{\zeta}^{\mathrm{gs}}\cdot\left(\frac{T^{\mathrm{s}}}{T^{\mathrm{g}}}\boldsymbol{v}^{\mathrm{g}}-\boldsymbol{v}^{\mathrm{s}}\right)+\left(\frac{\partial a^{\mathrm{l}}}{\partial\epsilon^{\mathrm{l}}}\boldsymbol{v}^{\mathrm{l}}-\frac{\partial a^{\mathrm{s}}}{\partial\epsilon^{\mathrm{s}}}\boldsymbol{v}^{\mathrm{s}}\right)\cdot\boldsymbol{\zeta}^{\mathrm{ls}}\cdot\left(\frac{T^{\mathrm{s}}}{T^{\mathrm{l}}}\boldsymbol{v}^{\mathrm{l}}-\boldsymbol{v}^{\mathrm{s}}\right)+\left(\frac{\partial a^{\mathrm{g}}}{\partial\epsilon^{\mathrm{g}}}-\frac{\partial a^{\mathrm{s}}}{\partial\epsilon^{\mathrm{s}}}\right)\frac{T^{\mathrm{s}}-T^{\mathrm{g}}}{R_{\mathrm{K}}^{\mathrm{gs}}}+\left(\frac{\partial a^{\mathrm{l}}}{\partial\epsilon^{\mathrm{l}}}-\frac{\partial a^{\mathrm{s}}}{\partial\epsilon^{\mathrm{s}}}\right)\frac{T^{\mathrm{s}}-T^{\mathrm{l}}}{R_{\mathrm{K}}^{\mathrm{ls}}}\\
&\quad-\frac{\partial a^{\mathrm{g}}}{\partial\epsilon^{\mathrm{g}}}\left(\lambda^{\mathrm{g}}\frac{\partial T^{\mathrm{g}}}{\partial\boldsymbol{r}}\cdot\boldsymbol{n}-\frac{\boldsymbol{v}^{\mathrm{g}^2}}{2}\Lambda\xi^{\mathrm{gl}}\right)+\frac{\partial a^{\mathrm{l}}}{\partial\epsilon^{\mathrm{l}}}\left(\lambda^{\mathrm{l}}\frac{\partial T^{\mathrm{l}}}{\partial\boldsymbol{r}}\cdot\boldsymbol{n}-\frac{\boldsymbol{v}^{\mathrm{l}^2}}{2}\Lambda\xi^{\mathrm{gl}}\right),
\end{aligned}\tag{41}$$

with the following driving force for the solute release process:

$$\xi^{\mathrm{gl}}=\frac{\partial s^{\mathrm{g}}}{\partial\rho^{\mathrm{g}}}+\frac{1}{T^{\mathrm{g}}}\frac{\boldsymbol{v}^{\mathrm{g}^2}}{2}-\frac{\partial s^{\mathrm{l}}}{\partial\rho^{\mathrm{l}}}-\frac{1-c^{\mathrm{l}}}{\rho^{\mathrm{l}}}\frac{\partial s^{\mathrm{l}}}{\partial c^{\mathrm{l}}}-\frac{1}{T^{\mathrm{l}}}\frac{\boldsymbol{v}^{\mathrm{l}^2}}{2}.\tag{42}$$

This driving force can be expressed in a more intuitive way in terms of chemical potentials,

$$\xi^{\mathrm{gl}}=-\frac{\tilde{\mu}^{\mathrm{g}}}{T^{\mathrm{g}}}+\frac{\tilde{\mu}^{\mathrm{l}}}{T^{\mathrm{l}}},\tag{43}$$

where $\tilde{\mu}^{\mathrm{g}}$ is the velocity-modified chemical potential in the gas and $\tilde{\mu}^{\mathrm{l}}$ is the velocity-modified chemical potential of the solute particles in the two-component liquid. As before, the normal unit vector $\boldsymbol{n}$ in the interfacial contributions points from V^{g} into V^{l}.

Equation (41) does not only imply the time-evolution equations for all interfacial variables but also boundary conditions for the bulk variables. Consistent equations for all observables A of the form (1) can only be obtained if, on the right-hand side of Eq. (41), all terms involving derivatives of the bulk densities a^{g} and a^{l} with respect to the independent bulk variables vanish. We thus obtain one boundary condition for each of the bulk variables,

$$\Lambda\xi^{\mathrm{gl}}=-\rho^{\mathrm{g}}(\boldsymbol{v}^{\mathrm{g}}-\boldsymbol{v}^{\mathrm{s}})\cdot\boldsymbol{n},\tag{44}$$

$$\Lambda\xi^{\mathrm{gl}}=-\rho^{\mathrm{l}}(\boldsymbol{v}^{\mathrm{l}}-\boldsymbol{v}^{\mathrm{s}})\cdot\boldsymbol{n},\tag{45}$$

$$\Lambda\xi^{\mathrm{gl}}=-\frac{\tilde{D}^{\mathrm{l}}}{1-c^{\mathrm{l}}}\boldsymbol{n}\cdot\frac{\partial}{\partial\boldsymbol{r}}\left(\frac{1}{\rho^{\mathrm{l}}}\frac{\partial s^{\mathrm{l}}(\rho^{\mathrm{l}},\epsilon^{\mathrm{l}},c^{\mathrm{l}})}{\partial c^{\mathrm{l}}}\right),\tag{46}$$

$$\boldsymbol{\zeta}^{\mathrm{gs}}\cdot\left(\frac{T^{\mathrm{s}}}{T^{\mathrm{g}}}\boldsymbol{v}^{\mathrm{g}}-\boldsymbol{v}^{\mathrm{s}}\right)=[\boldsymbol{M}^{\mathrm{g}}(\boldsymbol{v}^{\mathrm{g}}-\boldsymbol{v}^{\mathrm{s}})-(2\eta^{\mathrm{g}}\hat{\boldsymbol{\kappa}}^{\mathrm{g}}+\kappa^{\mathrm{g}}\operatorname{tr}\boldsymbol{\kappa}^{\mathrm{g}}\mathbf{1})]\cdot\boldsymbol{n},\tag{47}$$

$$\boldsymbol{\zeta}^{\mathrm{ls}}\cdot\left(\frac{T^{\mathrm{s}}}{T^{\mathrm{l}}}\boldsymbol{v}^{\mathrm{l}}-\boldsymbol{v}^{\mathrm{s}}\right)=-[\boldsymbol{M}^{\mathrm{l}}(\boldsymbol{v}^{\mathrm{l}}-\boldsymbol{v}^{\mathrm{s}})-(2\eta^{\mathrm{l}}\hat{\boldsymbol{\kappa}}^{\mathrm{l}}+\kappa^{\mathrm{l}}\operatorname{tr}\boldsymbol{\kappa}^{\mathrm{l}}\mathbf{1})]\cdot\boldsymbol{n},\tag{48}$$

$$\begin{aligned}\frac{T^{\mathrm{s}}-T^{\mathrm{g}}}{R_{\mathrm{K}}^{\mathrm{gs}}}&=-\left(\epsilon^{\mathrm{g}}+p^{\mathrm{g}}+\frac{1}{2}\rho^{\mathrm{g}}\boldsymbol{v}^{\mathrm{g}^2}\right)(\boldsymbol{v}^{\mathrm{g}}-\boldsymbol{v}^{\mathrm{s}})\cdot\boldsymbol{n}+\lambda^{\mathrm{g}}\frac{\partial T^{\mathrm{g}}}{\partial\boldsymbol{r}}\cdot\boldsymbol{n}\\&\quad+\boldsymbol{v}^{\mathrm{g}}\cdot(2\eta^{\mathrm{g}}\hat{\boldsymbol{\kappa}}^{\mathrm{g}}+\kappa^{\mathrm{g}}\operatorname{tr}\boldsymbol{\kappa}^{\mathrm{g}}\mathbf{1})\cdot\boldsymbol{n},\end{aligned}\tag{49}$$

$$\begin{aligned}\frac{T^{\mathrm{s}}-T^{\mathrm{l}}}{R_{\mathrm{K}}^{\mathrm{ls}}}&=\left(\epsilon^{\mathrm{l}}+p^{\mathrm{l}}+\frac{1}{2}\rho^{\mathrm{l}}\boldsymbol{v}^{\mathrm{l}^2}\right)(\boldsymbol{v}^{\mathrm{l}}-\boldsymbol{v}^{\mathrm{s}})\cdot\boldsymbol{n}-\lambda^{\mathrm{l}}\frac{\partial T^{\mathrm{l}}}{\partial\boldsymbol{r}}\cdot\boldsymbol{n}\\&\quad-\boldsymbol{v}^{\mathrm{l}}\cdot(2\eta^{\mathrm{l}}\hat{\boldsymbol{\kappa}}^{\mathrm{l}}+\kappa^{\mathrm{l}}\operatorname{tr}\boldsymbol{\kappa}^{\mathrm{l}}\mathbf{1})\cdot\boldsymbol{n}.\end{aligned}\tag{50}$$

The boundary conditions (44) and (45) can be combined into the "jump mass balance"

$$\rho^{\mathrm{g}}(\boldsymbol{v}^{\mathrm{g}}-\boldsymbol{v}^{\mathrm{s}})\cdot\boldsymbol{n}=\rho^{\mathrm{l}}(\boldsymbol{v}^{\mathrm{l}}-\boldsymbol{v}^{\mathrm{s}})\cdot\boldsymbol{n},\tag{51}$$

which expresses the notion that the interface cannot store any mass. Instead of Eq. (51), we actually have the stronger gauge invariance condition (3). In addition, $\boldsymbol{v}^{\mathrm{s}}$ can be eliminated between Eqs. (44) and (45) to obtain a relationship between bulk variables at the interface only,

$$\frac{\rho^{\mathrm{g}}\rho^{\mathrm{l}}}{\rho^{\mathrm{l}}-\rho^{\mathrm{g}}}(\boldsymbol{v}^{\mathrm{l}}-\boldsymbol{v}^{\mathrm{g}})\cdot\boldsymbol{n}=\Lambda\xi^{\mathrm{gl}}.\tag{52}$$

By choosing a^{s} in Eq. (41) as ρ^{s}, $\boldsymbol{M}^{\mathrm{s}}$, and $\boldsymbol{\epsilon}^{\mathrm{s}}$, we obtain the following evolution equations for the interfacial densities of excess mass, momentum, and internal energy:

$$\frac{\partial \rho^{\mathrm{s}}}{\partial t} + \frac{\partial}{\partial \boldsymbol{r}_{\|}} \cdot (\boldsymbol{v}_{\|}^{\mathrm{s}} \rho^{\mathrm{s}}) + w_n^{\mathrm{s}} \rho^{\mathrm{s}} \frac{\partial}{\partial \boldsymbol{r}_{\|}} \cdot \boldsymbol{n} = 0, \tag{53}$$

$$\begin{aligned}\frac{\partial \boldsymbol{M}^{\mathrm{s}}}{\partial t} + \frac{\partial}{\partial \boldsymbol{r}_{\|}} \cdot (\boldsymbol{v}_{\|}^{\mathrm{s}} \boldsymbol{M}^{\mathrm{s}}) + w_n^{\mathrm{s}} \boldsymbol{M}^{\mathrm{s}} \frac{\partial}{\partial \boldsymbol{r}_{\|}} \cdot \boldsymbol{n} = [\boldsymbol{M}^{\mathrm{g}}(\boldsymbol{v}^{\mathrm{g}} - \boldsymbol{v}^{\mathrm{s}}) - \boldsymbol{M}^{\mathrm{l}}(\boldsymbol{v}^{\mathrm{l}} \\ - \boldsymbol{v}^{\mathrm{s}})] \cdot \boldsymbol{n} - \frac{\partial p^{\mathrm{s}}}{\partial \boldsymbol{r}_{\|}} - (2\eta^{\mathrm{g}} \hat{\boldsymbol{\kappa}}^{\mathrm{g}} + \kappa^{\mathrm{g}} \operatorname{tr} \boldsymbol{\kappa}^{\mathrm{g}} \mathbf{1}) \cdot \boldsymbol{n} \\ + (2\eta^{\mathrm{l}} \hat{\boldsymbol{\kappa}}^{\mathrm{l}} + \kappa^{\mathrm{l}} \operatorname{tr} \boldsymbol{\kappa}^{\mathrm{l}} \mathbf{1}) \cdot \boldsymbol{n} + \boldsymbol{n} \left(p^{\mathrm{g}} - p^{\mathrm{l}} + p^{\mathrm{s}} \frac{\partial}{\partial \boldsymbol{r}_{\|}} \cdot \boldsymbol{n} \right),\end{aligned} \tag{54}$$

and

$$\begin{aligned}\frac{\partial \boldsymbol{\epsilon}^{\mathrm{s}}}{\partial t} + \frac{\partial}{\partial \boldsymbol{r}_{\|}} \cdot (\boldsymbol{v}_{\|}^{\mathrm{s}} \boldsymbol{\epsilon}^{\mathrm{s}}) + w_n^{\mathrm{s}} \boldsymbol{\epsilon}^{\mathrm{s}} \frac{\partial}{\partial \boldsymbol{r}_{\|}} \cdot \boldsymbol{n} = - p^{\mathrm{s}} \left(\frac{\partial}{\partial \boldsymbol{r}_{\|}} \cdot \boldsymbol{v}_{\|}^{\mathrm{s}} + w_n^{\mathrm{s}} \frac{\partial}{\partial \boldsymbol{r}_{\|}} \cdot \boldsymbol{n} \right) \\ - \left(\lambda^{\mathrm{g}} \frac{\partial T^{\mathrm{g}}}{\partial \boldsymbol{r}} - \lambda^{\mathrm{l}} \frac{\partial T^{\mathrm{l}}}{\partial \boldsymbol{r}} \right) \cdot \boldsymbol{n} + \left[\frac{1}{2} \rho^{\mathrm{g}} (\boldsymbol{v}^{\mathrm{g}} - \boldsymbol{v}^{\mathrm{s}})^2 + \epsilon^{\mathrm{g}} + p^{\mathrm{g}} \right] \\ \times (\boldsymbol{v}^{\mathrm{g}} - \boldsymbol{v}^{\mathrm{s}}) \cdot \boldsymbol{n} - \left[\frac{1}{2} \rho^{\mathrm{l}} (\boldsymbol{v}^{\mathrm{l}} - \boldsymbol{v}^{\mathrm{s}})^2 + \epsilon^{\mathrm{l}} + p^{\mathrm{l}} \right] (\boldsymbol{v}^{\mathrm{l}} - \boldsymbol{v}^{\mathrm{s}}) \cdot \boldsymbol{n} \\ - (\boldsymbol{v}^{\mathrm{g}} - \boldsymbol{v}^{\mathrm{s}}) \cdot (2\eta^{\mathrm{g}} \hat{\boldsymbol{\kappa}}^{\mathrm{g}} + \kappa^{\mathrm{g}} \operatorname{tr} \boldsymbol{\kappa}^{\mathrm{g}} \mathbf{1}) \cdot \boldsymbol{n} \\ + (\boldsymbol{v}^{\mathrm{l}} - \boldsymbol{v}^{\mathrm{s}}) \cdot (2\eta^{\mathrm{l}} \hat{\boldsymbol{\kappa}}^{\mathrm{l}} + \kappa^{\mathrm{l}} \operatorname{tr} \boldsymbol{\kappa}^{\mathrm{l}} 1) \cdot \boldsymbol{n}.\end{aligned} \tag{55}$$

The pressure terms in Eq. (55) for the energy describe the change of area due to flow within the interface and the change of area due to the motion of the interface, respectively. We thus see how interfacial tension arises through the analog of the Gibbs-Duhem equation for the interface. By a further application of Eq. (41) to the mass of the solute species (10), we find the following evolution equation for the scalar mass fraction:

$$\rho^{\mathrm{s}} \left(\frac{\partial c^{\mathrm{l}}}{\partial t} + \boldsymbol{v}_{\|}^{\mathrm{s}} \cdot \frac{\partial c^{\mathrm{l}}}{\partial \boldsymbol{r}_{\|}} \right) = 0. \tag{56}$$

Equations (53)–(56) are balance equations for surface excess quantities in terms of the bulk fluxes of the respective quantities.

The vanishing right-hand side of Eq. (53) expresses the fact that ρ^{s} is a small and ambiguous variable. The interface cannot take up mass, the occurrence of ρ^{s} is only a matter of choosing the precise location of the interface. Also Eq. (56) expresses the inability of the interface to accumulate mass.

As momentum cannot be stored in the interface either, also $\boldsymbol{M}^{\mathrm{s}}$ is a small ambiguous variable and both sides of Eq. (54) must vanish. We thus obtain the further boundary condition ("jump linear momentum balance"),

$$\begin{aligned}\boldsymbol{M}^{\mathrm{l}}(\boldsymbol{v}^{\mathrm{l}} - \boldsymbol{v}^{\mathrm{s}}) \cdot \boldsymbol{n} - (2\eta^{\mathrm{l}} \hat{\boldsymbol{\kappa}}^{\mathrm{l}} + \kappa^{\mathrm{l}} \operatorname{tr} \boldsymbol{\kappa}^{\mathrm{l}} \mathbf{1}) \cdot \boldsymbol{n} + p^{\mathrm{l}} \boldsymbol{n} = \boldsymbol{M}^{\mathrm{g}}(\boldsymbol{v}^{\mathrm{g}} - \boldsymbol{v}^{\mathrm{s}}) \cdot \boldsymbol{n} \\ - (2\eta^{\mathrm{g}} \hat{\boldsymbol{\kappa}}^{\mathrm{g}} + \kappa^{\mathrm{g}} \operatorname{tr} \boldsymbol{\kappa}^{\mathrm{g}} \mathbf{1}) \cdot \boldsymbol{n} + p^{\mathrm{g}} \boldsymbol{n} - \frac{\partial p^{\mathrm{s}}}{\partial \boldsymbol{r}_{\|}} + p^{\mathrm{s}} \boldsymbol{n} \frac{\partial}{\partial \boldsymbol{r}_{\|}} \cdot \boldsymbol{n}.\end{aligned} \tag{57}$$

The internal energy $\boldsymbol{\epsilon}^{\mathrm{s}}$ is a relevant interfacial variable. Its time evolution is governed by Eq. (55), and it implies all the information about T^{s}, p^{s}, and s^{s}. In particular, the time evolution of $\boldsymbol{\epsilon}^{\mathrm{s}}$ is consistent with the natural entropy balance

$$\begin{aligned}\frac{\partial s^{\mathrm{s}}}{\partial t} + \frac{\partial}{\partial \boldsymbol{r}_{\|}} \cdot (\boldsymbol{v}_{\|}^{\mathrm{s}} s^{\mathrm{s}}) + w_n^{\mathrm{s}} s^{\mathrm{s}} \frac{\partial}{\partial \boldsymbol{r}_{\|}} \cdot \boldsymbol{n} \\ = \left[s^{\mathrm{g}} (\boldsymbol{v}^{\mathrm{g}} - \boldsymbol{v}^{\mathrm{s}}) - s^{\mathrm{l}} (\boldsymbol{v}^{\mathrm{l}} - \boldsymbol{v}^{\mathrm{s}}) - \frac{\lambda^{\mathrm{g}}}{T^{\mathrm{g}}} \frac{\partial T^{\mathrm{g}}}{\partial \boldsymbol{r}} + \frac{\lambda^{\mathrm{l}}}{T^{\mathrm{l}}} \frac{\partial T^{\mathrm{l}}}{\partial \boldsymbol{r}} \right] \cdot \boldsymbol{n} \\ + \frac{1 - c^{\mathrm{l}}}{\rho^{\mathrm{l}}} \frac{\partial s^{\mathrm{l}}(\rho^{\mathrm{l}}, \epsilon^{\mathrm{l}}, c^{\mathrm{l}})}{\partial c^{\mathrm{l}}} \Lambda \xi^{\mathrm{gl}} + \left(\frac{T^{\mathrm{s}}}{T^{\mathrm{g}}} \boldsymbol{v}^{\mathrm{g}} - \boldsymbol{v}^{\mathrm{s}} \right) \cdot \frac{\boldsymbol{\zeta}^{\mathrm{gs}}}{T^{\mathrm{s}}} \cdot \left(\frac{T^{\mathrm{s}}}{T^{\mathrm{g}}} \boldsymbol{v}^{\mathrm{g}} \right. \\ \left. - \boldsymbol{v}^{\mathrm{s}} \right) + \left(\frac{T^{\mathrm{s}}}{T^{\mathrm{l}}} \boldsymbol{v}^{\mathrm{l}} - \boldsymbol{v}^{\mathrm{s}} \right) \cdot \frac{\boldsymbol{\zeta}^{\mathrm{ls}}}{T^{\mathrm{s}}} \cdot \left(\frac{T^{\mathrm{s}}}{T^{\mathrm{l}}} \boldsymbol{v}^{\mathrm{l}} - \boldsymbol{v}^{\mathrm{s}} \right) + \frac{(T^{\mathrm{g}} - T^{\mathrm{s}})^2}{T^{\mathrm{g}} T^{\mathrm{s}} R_{\mathrm{K}}^{\mathrm{gs}}} \\ + \frac{(T^{\mathrm{l}} - T^{\mathrm{s}})^2}{T^{\mathrm{l}} T^{\mathrm{s}} R_{\mathrm{K}}^{\mathrm{ls}}} + \Lambda (\xi^{\mathrm{gl}})^2,\end{aligned} \tag{58}$$

as can be shown by making use of the boundary conditions. In view of Eqs. (55) and (57), the interfacial pressure p^{s} must clearly be a relevant variable.

In principle, all the jump balances and boundary conditions of the present section can also be obtained from the traditional approaches to interfaces [22,23]. However, within the GENERIC approach, all evolution equations and boundary conditions arise from a single equation that automatically guarantees their completeness and thermodynamic consistency. In particular, we obtain a reliable and transparent entropy balance equation. Instead of our separate equations (51) and (52), a combined jump mass balance occurs in Eq. (1.3.5–4) of [22] or in Eq. (16.1–8) of [23]. The splitting into two equations results from a strict rather than approximate implementation of gauge invariance, where the underlying ideas have essentially been discussed in terms of order-of-magnitude arguments in the paragraph after Eq. (16.1–8) of [23]. A similar splitting leads from the standard form (54) of the jump momentum balance to the boundary condition (57).

III. SINGLE SPHERICAL BUBBLE

We now focus on a single spherical bubble in an infinite solution. We hence specialize our equations to the case for which the velocity field has only a radial component and all hydrodynamic fields depend only on the distance from the center. This simplification allows us to analyze the nature and the completeness of the boundary conditions in more detail.

A. Full equations

We describe the spherical gas bubble by the three scalar fields $\rho^{\mathrm{g}}(r)$, $v^{\mathrm{g}}(r)$, and $T^{\mathrm{g}}(r)$, where v^{g} is the radial velocity component and r is the distance from the center of the bubble. The continuity equation for the mass density,

$$\frac{\partial \rho^{\mathrm{g}}}{\partial t} = - \frac{1}{r^2} \frac{\partial}{\partial r} (r^2 v^{\mathrm{g}} \rho^{\mathrm{g}}), \tag{59}$$

can be integrated to obtain an explicit expression for the velocity field in terms of the density field,

$$v^{\mathrm{g}}(r,t) = -\frac{1}{r^2\rho^{\mathrm{g}}(r,t)}\int_0^r r'^2\frac{\partial\rho^{\mathrm{g}}(r',t)}{\partial t}dr', \tag{60}$$

where the integration constant has been determined by assuming regularity at the origin.

The equation of motion for the radial velocity field becomes

$$\rho^{\mathrm{g}}\left(\frac{\partial v^{\mathrm{g}}}{\partial t} + v^{\mathrm{g}}\frac{\partial v^{\mathrm{g}}}{\partial r}\right) = \frac{4}{3}\frac{1}{r^3}\frac{\partial}{\partial r}\left[\eta^{\mathrm{g}} r^4\frac{\partial}{\partial r}\left(\frac{v^{\mathrm{g}}}{r}\right)\right] + \frac{\partial}{\partial r}\left[\kappa^{\mathrm{g}}\frac{1}{r^2}\frac{\partial}{\partial r}(r^2 v^{\mathrm{g}})\right] - \frac{\partial p^{\mathrm{g}}}{\partial r}. \tag{61}$$

The temperature equation reads as

$$\frac{\partial T^{\mathrm{g}}}{\partial t} = -v^{\mathrm{g}}\frac{\partial T^{\mathrm{g}}}{\partial r} - \frac{1}{\alpha_s^{\mathrm{g}}}\frac{1}{r^2}\frac{\partial}{\partial r}(r^2 v^{\mathrm{g}}) + \frac{1}{\rho^{\mathrm{g}}\hat{c}_V^{\mathrm{g}}}\left\{\frac{4}{3}\eta^{\mathrm{g}}\left[r\frac{\partial}{\partial r}\left(\frac{v^{\mathrm{g}}}{r}\right)\right]^2 + \kappa^{\mathrm{g}}\left[\frac{1}{r^2}\frac{\partial}{\partial r}(r^2 v^{\mathrm{g}})\right]^2 + \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\lambda^{\mathrm{g}}\frac{\partial T^{\mathrm{g}}}{\partial r}\right)\right\}, \tag{62}$$

where α_s^{g} is the adiabatic thermal expansivity and $\hat{c}_V^{\mathrm{g}}$ is the heat capacity per unit mass for the gas.

We describe the bulk liquid phase by the four scalar fields $\rho^{\mathrm{l}}(r)$, $v^{\mathrm{l}}(r)$, $T^{\mathrm{l}}(r)$, and $c^{\mathrm{l}}(r)$. The continuity equation for the mass density,

$$\frac{\partial\rho^{\mathrm{l}}}{\partial t} = -\frac{1}{r^2}\frac{\partial}{\partial r}(r^2 v^{\mathrm{l}}\rho^{\mathrm{l}}), \tag{63}$$

and the equation of motion for the radial velocity field,

$$\rho^{\mathrm{l}}\left(\frac{\partial v^{\mathrm{l}}}{\partial t} + v^{\mathrm{l}}\frac{\partial v^{\mathrm{l}}}{\partial r}\right) = \frac{4}{3}\frac{1}{r^3}\frac{\partial}{\partial r}\left[\eta^{\mathrm{l}} r^4\frac{\partial}{\partial r}\left(\frac{v^{\mathrm{l}}}{r}\right)\right] + \frac{\partial}{\partial r}\left[\kappa^{\mathrm{l}}\frac{1}{r^2}\frac{\partial}{\partial r}(r^2 v^{\mathrm{l}})\right] - \frac{\partial p^{\mathrm{l}}}{\partial r}, \tag{64}$$

are the direct analogs of Eqs. (59) and (61). To obtain the proper spherically symmetric temperature equation for the two-component liquid, we start from the general temperature equation

$$\frac{\partial T^{\mathrm{l}}}{\partial t} = -\boldsymbol{v}^{\mathrm{l}}\cdot\frac{\partial T^{\mathrm{l}}}{\partial \boldsymbol{r}} - \frac{1}{\alpha_s^{\mathrm{l}}}\frac{\partial}{\partial \boldsymbol{r}}\cdot\boldsymbol{v}^{\mathrm{l}} + \frac{1}{\rho^{\mathrm{l}}\hat{c}_V^{\mathrm{l}}}\left[\frac{\partial\epsilon^{\mathrm{l}}}{\partial t} + \frac{\partial}{\partial \boldsymbol{r}}\cdot(\boldsymbol{v}^{\mathrm{l}}\epsilon^{\mathrm{l}}) + p^{\mathrm{l}}\frac{\partial}{\partial \boldsymbol{r}}\cdot\boldsymbol{v}^{\mathrm{l}}\right] - T^{\mathrm{l}2}\frac{\partial^2 s^{\mathrm{l}}}{\partial\epsilon^{\mathrm{l}}\,\partial c^{\mathrm{l}}}\left(\frac{\partial c^{\mathrm{l}}}{\partial t} + \boldsymbol{v}^{\mathrm{l}}\cdot\frac{\partial c^{\mathrm{l}}}{\partial \boldsymbol{r}}\right), \tag{65}$$

which can be obtained most conveniently by acting with the material time derivative on the definition of $1/T^{\mathrm{l}}$ in Eq. (8). For spherical symmetry, we thus obtain the following generalization of Eq. (62) for the two-component liquid phase:

$$\frac{\partial T^{\mathrm{l}}}{\partial t} = -v^{\mathrm{l}}\frac{\partial T^{\mathrm{l}}}{\partial r} - \frac{1}{\alpha_s^{\mathrm{l}}}\frac{1}{r^2}\frac{\partial}{\partial r}(r^2 v^{\mathrm{l}}) + \frac{1}{\rho^{\mathrm{l}}\hat{c}_V^{\mathrm{l}}}\left\{\frac{4}{3}\eta^{\mathrm{l}}\left[r\frac{\partial}{\partial r}\left(\frac{v^{\mathrm{l}}}{r}\right)\right]^2 + \kappa^{\mathrm{l}}\left[\frac{1}{r^2}\frac{\partial}{\partial r}(r^2 v^{\mathrm{l}})\right]^2 + \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\lambda^{\mathrm{l}}\frac{\partial T^{\mathrm{l}}}{\partial r}\right)\right\} - T^{\mathrm{l}2}\frac{\partial^2 s^{\mathrm{l}}}{\partial\epsilon^{\mathrm{l}}\,\partial c^{\mathrm{l}}}\left(\frac{\partial c^{\mathrm{l}}}{\partial t} + v^{\mathrm{l}}\frac{\partial c^{\mathrm{l}}}{\partial r}\right). \tag{66}$$

The material time evolution of c^{l} occurring in the last term is given by the diffusion equation

$$\frac{\partial c^{\mathrm{l}}}{\partial t} + v^{\mathrm{l}}\frac{\partial c^{\mathrm{l}}}{\partial r} = -\frac{1}{\rho^{\mathrm{l}} r^2}\frac{\partial}{\partial r}\left[r^2\tilde{D}^{\mathrm{l}}\frac{\partial}{\partial r}\left(\frac{1}{\rho^{\mathrm{l}}}\frac{\partial s^{\mathrm{l}}}{\partial c^{\mathrm{l}}}\right)\right]. \tag{67}$$

Let us now consider the boundary conditions for the seven hydrodynamic fields describing the gas and the liquid. For each field describing the gas, there is a boundary condition at $r=0$ because the conserved quantities cannot be accumulated at the origin. For each field describing the liquid, there is a boundary condition for $r\to\infty$ where the asymptotic conditions are assumed to be fixed. At the interface, we hence need only one boundary condition for each of the fields governed by partial differential equations involving second-order derivatives, that is, for the variables v^{g}, T^{g} and v^{l}, T^{l}, and c^{l}.

The boundary conditions for v^{g} and v^{l} at $r=R$ are given by Eqs. (52) and (57),

$$v^{\mathrm{g}} - v^{\mathrm{l}} = -\left(\frac{1}{\rho^{\mathrm{g}}} - \frac{1}{\rho^{\mathrm{l}}}\right)\Lambda\xi^{\mathrm{gl}}, \tag{68}$$

and

$$\frac{4}{3}\eta^{\mathrm{l}} r\frac{\partial}{\partial r}\left(\frac{v^{\mathrm{l}}}{r}\right) + \frac{\kappa^{\mathrm{l}}}{r^2}\frac{\partial}{\partial r}(r^2 v^{\mathrm{l}}) - p^{\mathrm{l}} = \frac{4}{3}\eta^{\mathrm{g}} r\frac{\partial}{\partial r}\left(\frac{v^{\mathrm{g}}}{r}\right) + \frac{\kappa^{\mathrm{g}}}{r^2}\frac{\partial}{\partial r}(r^2 v^{\mathrm{g}}) - p^{\mathrm{g}} - \frac{2p^{\mathrm{s}}}{R} + (v^{\mathrm{g}} - v^{\mathrm{l}})\Lambda\xi^{\mathrm{gl}}, \tag{69}$$

where the bubble radius R can be determined from Eq. (45),

$$\frac{dR}{dt} = v^{\mathrm{s}} = v^{\mathrm{l}}(R) + \frac{1}{\rho^{\mathrm{l}}}\Lambda\xi^{\mathrm{gl}}. \tag{70}$$

In addition to this equation for v^{s}, the other relevant interfacial variable, for example, the temperature of the interface T^{s}, can be obtained from Eq. (55).

Equation (46) serves as a boundary condition for c^{l}. The boundary conditions for T^{g} and T^{l} at $r=R$ are given by Eqs. (49) and (50) for the case of spherical symmetry.

At this point, all available equations except Eqs. (47) and (48) have been used. What is the significance of these remaining two equations? Actually, these two equations play the role of constraints. The irreversible momentum transfer between the bulk phases and the interface is a subtle process and cannot be described by simple given friction tensors $\boldsymbol{\zeta}^{\mathrm{gs}}$ and $\boldsymbol{\zeta}^{\mathrm{ls}}$. Rather, the momentum transfer at the interface depends on all the details of the local stress situation, and Eqs. (47) and (48) can be used to determine the effective friction tensors such that the two bulk phases stay in contact at the interface. Actually, one can solve the other equations without even calculating these effective friction tensors.

Finally, let us consider the isothermal case. This special case can be obtained by taking the limit of infinite thermal conductivities and vanishing Kapitza resistances. We assume that, in this limit, the dissipation due to the corresponding processes vanishes. If all temperatures $T^{\mathrm{s}}=T^{\mathrm{g}}=T^{\mathrm{l}}$ are equal to the externally specified one, the boundary conditions (49) and (50) become irrelevant because they are solved by vanishingly small perturbations of the constant-temperature field.

In summary, we have the time-evolution equations (59), (61), and (62) in the gas bubble, Eqs. (63), (64), (66), and (67) in the two-component liquid. The evolution of the relevant interfacial properties is given by Eqs. (55) and (70). For the velocity field, we have the boundary conditions (68) and (69), and the required boundary conditions for the temperature field are given by Eqs. (49) and (50).

B. Simplified equations

We consider the growth of a single-component spherical gas bubble of radius $R(t)$ surrounded by a liquid of infinite extent. Bubble growth is driven by the isothermal diffusion of a volatile solute dissolved in the liquid. There is mass transfer across the interface at $r=R(t)$ that separates the bubble and liquid phases, and bubble growth is induced by a pressure reduction in the liquid at $t=0^-$ from p_0 to p_∞ causing the liquid to become supersaturated; bubble collapse is induced by a pressure increase in the liquid at $t=0^-$ from p_0 to p_∞ causing the liquid to become undersaturated. For $t<0$, the system is assumed to be in mechanical, thermal, and chemical equilibrium, and a bubble with radius R_0 exists as a result of thermal fluctuations. The initial solute composition in the liquid is $c^{\mathrm{l}}(r,0)=c_0=Kp_0$, where K is a version of Henry's law constant, the initial temperature is T_0, and both the gas and liquid are at rest. The previously given version $k_{\mathrm{H,cc}}$ of Henry's law constant is given by $k_{\mathrm{H,cc}}=K\rho_0 k_{\mathrm{B}} T_0/m$, where k_{B} is Boltzmann's constant and m is the mass of a gas particle. In the time period from $t=0^-$ to $t=0$, corresponding to the time for pressure wave to propagate through the liquid, the pressure in the liquid becomes uniform at p_∞. Therefore, the pressure in the liquid is given by $p^{\mathrm{l}}=p_\infty$ and the density is given by $\rho^{\mathrm{l}}=\rho_0$. We are interested in developing models that describe diffusion-induced bubble growth or collapse in liquids from an initial radius of R_0. Consequently, it is appropriate to use R_0 to scale length and the mass diffusivity to scale the relationship between time and length.

In view of the bubble growth phenomenon of interest just described, we make the following simplifying assumptions. *Overall*: spherical symmetry, negligible fluid inertia, negligible body forces, local equilibrium in each subsystem, absence of chemical reactions, position-independent transport coefficients, constant interfacial tension, vanishing Kapitza resistances for the heat transfer between the different subsystems, and negligible radiative heat transfer;*gas bubble*: mechanical equilibrium, infinite thermal conductivity, and vanishing bulk viscosity; *supersaturated liquid*: mechanical equilibrium, infinite thermal conductivity, and ideal solution entropy.

According to the discussion of the preceding subsection, the assumption of infinite thermal conductivities and vanishing Kapitza resistances leads to the isothermal situation $T^{\mathrm{s}}=T^{\mathrm{g}}=T^{\mathrm{l}}=T_0$.

In the uniformly expanding gas bubble, the density $\rho^{\mathrm{g}}(t)$ depends on time only and, at given temperature, it is equivalent to the pressure at the boundary. With the above assumptions, the momentum and energy balances are satisfied identically and, according to Eq. (60), the continuity equation implies the homogeneous radial velocity field,

$$v^{\mathrm{g}}(r,t)=-\frac{1}{3}r\frac{1}{\rho^{\mathrm{g}}(t)}\frac{d\rho^{\mathrm{g}}(t)}{dt}. \tag{71}$$

In the supersaturated liquid pushed away by the growing bubble, we have an inhomogeneous equibiaxial extensional flow situation (two extensional rates coincide for symmetry reasons). The dissipative stress tensor decays as r^{-3}, and the velocity field is of the form

$$v^{\mathrm{l}}(r,t)=\frac{f(t)}{r^2}, \tag{72}$$

where the function $f(t)$ needs to be determined from the boundary conditions at the interface to the bubble. For such a velocity field, the density ρ^{l} is independent of both position and time. This does not exclude the possibility of a changing density in response to an initial pressure jump, which could be applied to produce a supersaturated liquid (we merely do not resolve the resulting propagation of sound waves through the liquid). As in the gas bubble, we have a uniform temperature $T^{\mathrm{l}}(t)$ to be determined from the boundary conditions.

For the entropy, we assume ideal-gas behavior,

$$s^{\mathrm{g}}(\rho^{\mathrm{g}},\epsilon^{\mathrm{g}})=\frac{1}{2}\frac{k_{\mathrm{B}}}{m}\rho^{\mathrm{g}}\ln\left(\frac{{\epsilon^{\mathrm{g}}}^{3}}{{\rho^{\mathrm{g}}}^{5}}\right), \tag{73}$$

where, strictly speaking, a proper constant factor should be introduced to make the argument of the logarithm dimensionless, and ideal solution behavior,

$$s^{\mathrm{l}}(\rho^{\mathrm{l}},\epsilon^{\mathrm{l}},c^{\mathrm{l}})=\tilde{s}^{\mathrm{l}}(\rho^{\mathrm{l}},\epsilon^{\mathrm{l}})-\frac{k_{\mathrm{B}}}{m}\rho^{\mathrm{l}}c^{\mathrm{l}}\ln c^{\mathrm{l}}, \tag{74}$$

which implies that also $p^{\mathrm{l}}=p_\infty$ is independent of both position and time. After neglecting the inertial terms, we obtain from Eq. (42),

$$c^{\mathrm{l}}(R)=Kp^{\mathrm{g}}\exp\left\{\frac{m}{k_{\mathrm{B}}}\xi^{\mathrm{gl}}\right\}. \tag{75}$$

Henry's law is recovered under equilibrium conditions, that is, for $\xi^{\mathrm{gl}}=0$. For a supersaturated liquid, $c_0>Kp_\infty$, and for an undersaturated liquid, $c_0<Kp_\infty$. The only evolution equation that remains to be solved in the bulk is obtained from Eqs. (67) and (72),

$$\frac{\partial c^{\mathrm{l}}}{\partial t}=-\frac{f}{r^2}\frac{\partial c^{\mathrm{l}}}{\partial r}+\frac{D^{\mathrm{l}}}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial c^{\mathrm{l}}}{\partial r}\right), \tag{76}$$

where we have introduced the constant diffusion coefficient D^{l},

$$D^{\mathrm{l}}=\frac{k_{\mathrm{B}}\tilde{D}^{\mathrm{l}}}{m\rho^{\mathrm{l}}c^{\mathrm{l}}}. \tag{77}$$

The further simplified boundary conditions are written as follows. Equation (70) can be rewritten as

$$\frac{dR}{dt} = \frac{f}{R^2} + \frac{1}{\rho_0}\Lambda \xi^{\mathrm{gl}}, \qquad (78)$$

and the additional jump mass balance (68) combined with Eqs. (71) and (72) becomes

$$\frac{dp^{\mathrm{g}}}{dt} = \frac{3}{R}\left[\left(1 - \frac{\rho^{\mathrm{g}}}{\rho_0}\right)\Lambda \xi^{\mathrm{gl}} - \rho^{\mathrm{g}}\frac{f}{R^2}\right]. \qquad (79)$$

Using the ideal-gas law for the pressure implied by Eq. (73), we can rewrite Eq. (79) as follows:

$$\frac{dp^{\mathrm{g}}}{dt} = \frac{3}{R}\left[\left(\frac{k_{\mathrm{B}}T_0}{m}\rho_0 - p^{\mathrm{g}}\right)\frac{\Lambda}{\rho_0}\xi^{\mathrm{gl}} - p^{\mathrm{g}}\frac{f}{R^2}\right]. \qquad (80)$$

In these equations, f is obtained from the jump momentum balance (69) after inserting the velocity fields (71) and (72),

$$\frac{4}{R^3}\eta^{\mathrm{l}} f = p^{\mathrm{g}} - p_\infty + \frac{2}{R}p^{\mathrm{s}}, \qquad (81)$$

where inertial effects have been neglected, and, following standard praxis, the interfacial tension $-p^{\mathrm{s}}$ is assumed to be a positive constant. Finally, the nonequilibrium driving force variable ξ^{gl} is obtained by combining Eqs. (46), (74), (75), and (77),

$$\xi^{\mathrm{gl}} = \frac{1}{\Lambda}\frac{\rho_0 D^{\mathrm{l}}}{1 - Kp^{\mathrm{g}}\exp\{m\xi^{\mathrm{gl}}/k_{\mathrm{B}}\}}\left.\frac{\partial c^{\mathrm{l}}}{\partial r}\right|_{r=R}. \qquad (82)$$

If one assumes chemical equilibrium at the interface ($\xi^{\mathrm{gl}} = 0$), the gas pressure p^{g} determines the composition at the interface $c^{\mathrm{l}}(R)$ by the equality of chemical potentials (Henry's law), and we recover the equations of [20]. In the absence of chemical equilibrium, the relationship between $c^{\mathrm{l}}(R)$ and p^{g} depends on ξ^{gl}, which is obtained from Eq. (82).

C. Numerical results

For our numerical solution procedure, we evolve the variables c^{l}, R, and p^{g} according to the evolution equations (76), (78), and (80), respectively. The initial conditions are given by c_0, R_0, and $p_\infty - 2p^{\mathrm{s}}/R_0$. The boundary condition for c^{l} for $r \to \infty$ is c_0, and for $r = R$ is given by Eq. (75). Equations (81) and (82) determine the values of the auxiliary variables f and ξ^{gl} in the evolution equations. This system of equations contains nine parameters $(R_0, \rho_0, p_\infty, p^{\mathrm{s}}, c_0, K, \Lambda/m, D^{\mathrm{l}}, \eta^{\mathrm{l}})$, which we consider to be constant that can be used to form the six dimensionless parameters listed in Table II. Five of these parameters $(N_{\mathrm{A}}, N_{\mathrm{B}}/N_{\mathrm{A}}, N_{\mathrm{C}}, N_{\mathrm{K}}, N_{\mathrm{T}})$ have been introduced in previous studies [20,21]. The driving force for phase change is given by N_{A}, which is positive for bubble growth and negative for bubble collapse. The ratio $N_{\mathrm{B}}/N_{\mathrm{A}}$ gives the ratio of a characteristic gas density to the liquid density and is fixed at a value of 0.001. The parameter N_{K} is a dimensionless Henry's law constant and is specified such that $|1 - N_{\mathrm{K}}| \approx 1$. The value of the dimensionless surface tension is fixed $N_{\mathrm{C}} = 0.5$, and a product of transport coefficients has a fixed value $N_{\mathrm{T}} = 0.1$. Diffusion-controlled bubble growth/collapse occurs when interfacial and viscous effects are neglected ($N_{\mathrm{C}} = N_{\mathrm{T}} = 0$). For diffusion-controlled bubble growth from a zero initial radius $R = 2\beta\sqrt{D^{\mathrm{l}}t/R_0^2}$, where $\beta = \beta(N_{\mathrm{A}}, N_{\mathrm{B}}/N_{\mathrm{A}})$ [17]. The additional dimensionless parameter N_Λ in Table II, through Eq. (82), controls the degree of departure from chemical equilibrium at the interface.

TABLE II. Dimensionless parameters.

Description	Definition
Driving force for phase change	$N_{\mathrm{A}} = \frac{\rho_0 k_{\mathrm{B}} T_0}{m p_\infty}\frac{c_0 - Kp_\infty}{1 - Kp_\infty}$
Ratio of gas to liquid density	$\frac{N_{\mathrm{B}}}{N_{\mathrm{A}}} = \frac{m p_\infty}{\rho_0 k_{\mathrm{B}} T_0}$
Interfacial tension	$N_{\mathrm{C}} = -\frac{p^{\mathrm{s}}}{p_\infty R_0}$
Henry's law constant	$N_{\mathrm{K}} = \frac{K p_\infty}{c_0}$
Transport coefficients	$N_{\mathrm{T}} = \frac{\eta^{\mathrm{l}} D^{\mathrm{l}}}{p_\infty R_0^2}$
Solute release rate	$N_\Lambda = \frac{\Lambda k_{\mathrm{B}} R_0}{m \rho_0 D^{\mathrm{l}}}$

The system of differential/algebraic equations was numerically integrated using a solver described in [32] and implemented using a software package known as ATHENA VISUAL STUDIO. To facilitate the numerical solution of the equations, the coordinate transformations developed by Duda and Vrentas [15,16] were implemented. Finally, the accuracy of the numerical solutions was verified by comparison with previously published results [15,16,19,20].

The evolution of the bubble radius and pressure with time during bubble growth are shown in Figs. 2 and 3, respectively. As a reference, we show in Fig. 2 the exact similarity solution $R = 2\beta\sqrt{D^{\mathrm{l}}t/R_0^2}$, which gives the asymptotic growth rate for $R/R_0 \gg 1$. Also shown in Figs. 2 and 3 is the diffusion-controlled case ($N_{\mathrm{C}} = N_{\mathrm{T}} = 0$), where viscous and interfacial forces are neglected. For the diffusion-induced cases shown in Figs. 2 and 3, viscous and interfacial forces retard bubble growth and increase the pressure within the bubble. The increase in bubble pressure, as shown by Eq. (75), causes the solute concentration at the interface to increase, thereby reducing the driving for mass transfer and retarding bubble growth [20].

We now examine the dynamic behavior of the variable $\xi^{\mathrm{gl}} = (\mu^{\mathrm{l}} - \mu^{\mathrm{g}})/T_0$, which indicates the deviation from chemi-

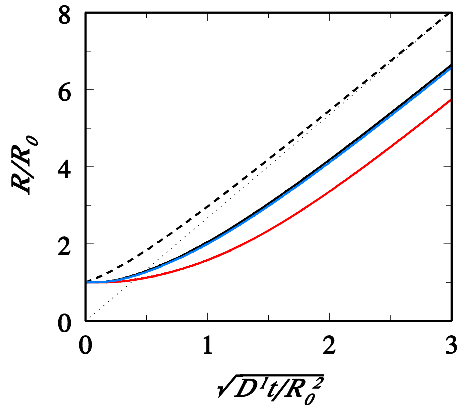

FIG. 2. (Color online) Bubble radius versus time during bubble growth for different values of the rate parameter N_Λ defined in Table II: solid lines from top to bottom are for $N_\Lambda \geq 0.1$, $N_\Lambda = 0.01$, and $N_\Lambda = 0.001$ (black, blueed in Table II are as follows: $N_{\mathrm{A}} = 1$, $N_{\mathrm{B}} = 0.001$, $N_{\mathrm{C}} = 0.5$, $N_{\mathrm{K}} = 0.1$, and $N_{\mathrm{T}} = 0.1$. Dashed black line is diffusion-controlled case ($N_{\mathrm{C}} = N_{\mathrm{T}} = 0$); thin dotted black line for $R = 2\beta\sqrt{D^{\mathrm{l}}t/R_0^2}$, with $\beta = 1.34$ [17].

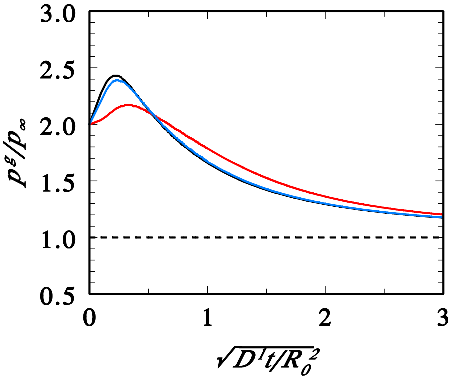

FIG. 3. (Color online) Bubble pressure versus time during bubble growth for different values of the rate parameter N_Λ defined in Table II: solid lines from top to bottom are for $N_\Lambda \geq 0.1$, $N_\Lambda = 0.01$, and $N_\Lambda = 0.001$ (black, blue, and red). Values of other parameters defined in Table II are as follows: $N_A = 1$, $N_B = 0.001$, $N_C = 0.5$, $N_K = 0.1$, and $N_T = 0.1$. Dashed black line is diffusion-controlled case ($N_C = N_T = 0$).

cal equilibrium at the interface, shown in Fig. 4. Since $\xi^{gl} > 0$, the chemical potential of the solute in the liquid phase is larger than in the gas phase. The equilibrium case is achieved when $N_B/N_\Lambda \ll 1$; ξ^{gl} shows a significant deviation from zero only at early times. For smaller values of N_Λ (larger values of N_B/N_Λ), larger departures from chemical equilibrium are observed, which in turn, increases the solute concentration at the interface as dictated by Eq. (75). As shown in Figs. 2 and 3, this retards bubble growth relative to the equilibrium case and leads to a decrease in the maximum bubble pressure. For all three cases shown in Fig. 4, ξ^{gl} appears to show a rapid initial decay followed by a significantly slower decay, which occurs shortly after the maximum in bubble pressure is reached.

It is of interest to examine the effect of nonequilibrium interfacial effects on the evolution of the bulk variable c^l. This is done in Fig. 5, which shows the same three cases shown in Figs. 2–4. For the equilibrium case ($N_\Lambda \geq 0.1$), the concentration gradient at the interface is large for all times. As discussed in a previous work [15], this stiffness has resulted in the reporting of inaccurate numerical solutions. As shown in Fig. 5, for increasing departures from equilibrium at the interface (decreasing values of N_Λ), the magnitude of the concentration gradient at the interface is reduced significantly, thereby, reducing the stiffness of the numerical problem to be solved.

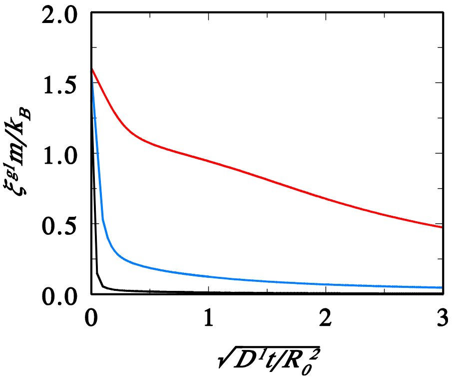

FIG. 4. (Color online) Interfacial driving force versus time during bubble growth for the cases shown in Figs. 2 and 3 (from bottom to top: black, blue, and red).

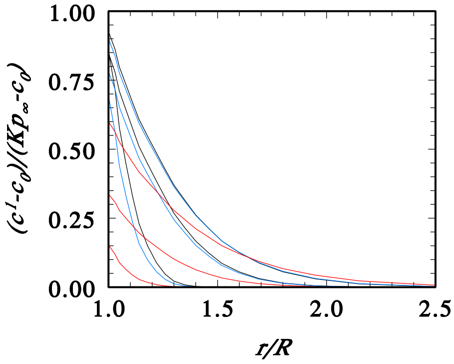

FIG. 5. (Color online) Composition profiles during bubble growth for the cases shown in Figs. 2 and 3 for different values of time: $D^l t/R_0^2 = 0.01, 0.1, 1$ (top to bottom).

For comparison, we show the evolution of the bubble radius and pressure with time during bubble growth in Figs. 6 and 7, respectively, for a larger driving force ($N_A = 10$), keeping $N_B/N_A (=0.001)$ and all other fixed parameters the same as those in earlier figures. We actually do this to achieve a situation in which the simplifying assumption $c^s = c^l$ can be justified. As before, viscous and interfacial forces retard bubble growth and increase the pressure within the bubble. However, because the growth rate is larger, the increase in bubble pressure is more pronounced. Similar to Fig. 4, the behavior of ξ^{gl} shown in Fig. 8 shows a rapid initial decrease followed by a much slower decrease just after the bubble pressure goes through a maximum. As with the smaller driving force case shown in Figs. 2–4, equilibrium at the interface for the larger growth rate is achieved when $N_B/N_\Lambda \ll 1$.

The evolution of the bubble radius and pressure with time during bubble collapse are shown in Figs. 9 and 10, respec-

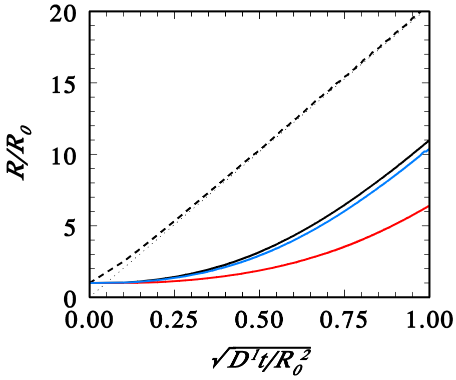

FIG. 6. (Color online) Bubble radius versus time during bubble growth for different values of the rate parameter N_Λ defined in Table II: solid lines from top to bottom are for $N_\Lambda \geq 1$, $N_\Lambda = 0.1$, and $N_\Lambda = 0.01$ (black, blue, and red). Values of other parameters defined in Table II are as follows: $N_A = 10$, $N_B = 0.01$, $N_C = 0.5$, $N_K = 0.1$, and $N_T = 0.1$. Dashed black line is diffusion-controlled case ($N_C = N_T = 0$); thin dotted black line for $R = 2\beta\sqrt{D^l t/R_0^2}$, with $\beta = 10.2$ [17].

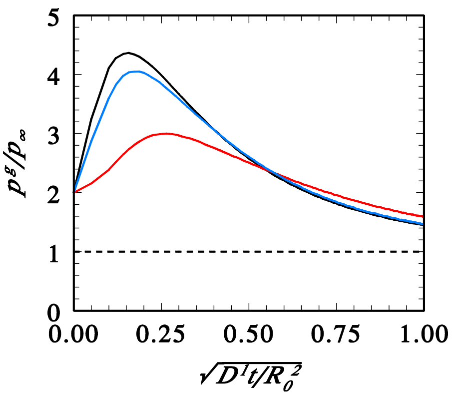

FIG. 7. (Color online) Bubble pressure versus time during bubble growth for different values of the rate parameter N_Λ defined in Table II: solid lines from top to bottom are for $N_\Lambda \geq 1$, $N_\Lambda = 0.1$, and $N_\Lambda = 0.01$ (black, blue, and red). Values of other parameters defined in Table II are as follows: $N_A = 10$, $N_B = 0.01$, $N_C = 0.5$, $N_K = 0.1$, and $N_T = 0.1$. Dashed black line is diffusion-controlled case ($N_C = N_T = 0$).

tively. The diffusion-controlled case ($N_C = N_T = 0$), where viscous and interfacial forces are neglected, is also shown in Figs. 9 and 10. As with bubble growth, viscous and interfacial forces increase the bubble pressure during diffusion-induced bubble collapse. For the equilibrium case ($N_\Lambda \geq 0.1$ for the case shown in Figs. 9 and 10), the bubble pressure shows a rapid initial decrease and then remains nearly constant until the bubble dissolves completely [19]. As shown by Eq. (75), the solute concentration at the interface increases with increasing bubble pressure; for bubble collapse, this increases the driving for mass transfer. However, as the bubble radius decreases, both viscous and interfacial forces increase and retard bubble collapse. Thus, for the equilibrium case shown in Figs. 9 and 10, the net result of these competing effects is to retard bubble collapse.

The dynamic behavior of ξ^{gl} during bubble collapse is shown in Fig. 11. Here, $\xi^{gl} < 0$, meaning the chemical potential of the solute in the liquid phase is smaller than in the gas phase. The equilibrium case is achieved when $N_\Lambda \gg N_B/N_A (N_\Lambda \geq 0.1)$; again, ξ^{gl} shows a significant deviation from zero only at early times. For smaller values of N_Λ, larger departures from chemical equilibrium are observed, which appear to track the behavior the bubble pressure shown in Fig. 10. Since $\xi^{gl} < 0$, nonequilibrium effects cause the solute concentration at the interface to decrease as dictated by Eq. (75), thereby, reducing the driving force for mass transfer. Hence, the increase in bubble pressure results in both a mechanical and chemical impedance to bubble collapse and dramatically increases the bubble lifetime as shown in Fig. 9.

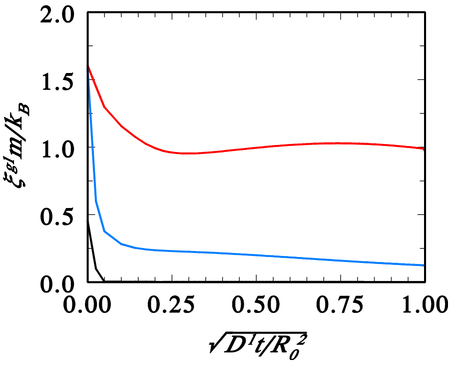

FIG. 8. (Color online) Interfacial driving force versus time during bubble growth for the cases shown in Figs. 6 and 7 (from bottom to top: black, blue, and red).

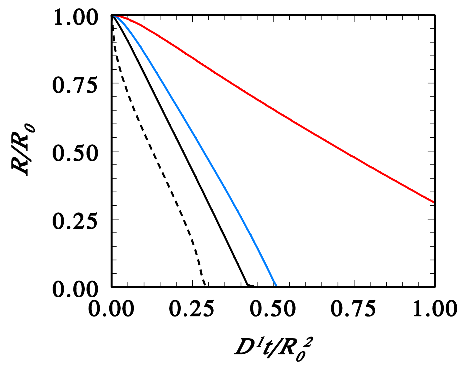

FIG. 9. (Color online) Bubble radius versus time during bubble collapse for different values of the rate parameter N_Λ defined in Table II: solid lines from bottom to top are for $N_\Lambda \geq 0.1$, $N_\Lambda = 0.01$, and $N_\Lambda = 0.001$ (black, blue, and red). Values of other parameters defined in Table II are as follows: $N_A = -1$, $N_B = -0.001$, $N_C = 0.5$, $N_K = 2$, and $N_T = 0.1$. Dashed black line is diffusion-controlled case ($N_C = N_T = 0$).

IV. SUMMARY AND CONCLUSIONS

We have extended the GENERIC framework of nonequilibrium thermodynamics to handle systems with moving interfaces. In order to obtain consistency between the thermodynamic evolution equation and the chain rule of functional calculus, we needed to introduce a moving interface normal transfer term. After introducing such a term, GENERIC provides all evolution equations and boundary conditions re-

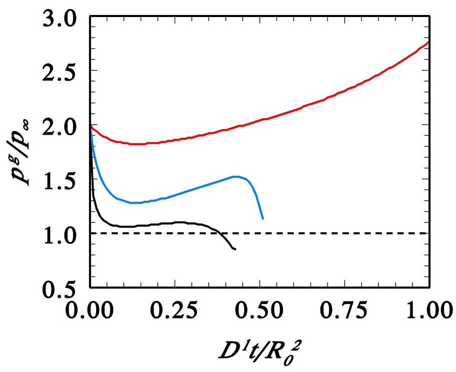

FIG. 10. (Color online) Bubble pressure versus time during bubble collapse for different values of the rate parameter N_Λ defined in Table II: solid lines from bottom to top are for $N_\Lambda \geq 0.1$, $N_\Lambda = 0.01$, and $N_\Lambda = 0.001$ (black, blue, and red). Values of other parameters defined in Table II are as follows: $N_A = -1$, $N_B = -0.001$, $N_C = 0.5$, $N_K = 2$, and $N_T = 0.1$. Dashed black line is diffusion-controlled case ($N_C = N_T = 0$).

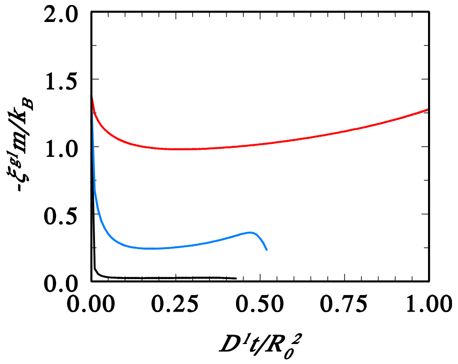

FIG. 11. (Color online) Interfacial driving force versus time during bubble collapse for the cases shown in Figs. 9 and 10 (from bottom to top: black, blue, and red).

quired for the system, as we have discussed in detail for a spherical gas bubble in a liquid. Whereas the same equations could be obtained from classical irreversible thermodynamics with the extra possibility of handling excess quantities at surfaces and interfaces through Heaviside and delta functions [3–5,25], the power and elegance of the GENERIC framework is obvious. For example, GENERIC can readily be applied to situations in which structural variables in addition to the hydrodynamic variables governed by the balance equations of the present paper become important.

In general, interfacial variables can be classified as either macroscopically relevant or ambiguous, depending on their sensitivity to microscopic displacements of the interface. We have added depth to such a distinction by introducing gauge transformations associated with these microscopic displacements of the interface. The physical predictions should be gauge invariant; however, for the formulation of thermodynamically consistent equations, it may be much more convenient or even essential to fall back on gauge-dependent variables. For example, for the proper formulation of the kinetic-energy contribution one needs to keep the ambiguous excess mass and momentum variables, even though only their ratio—the interface velocity—is macroscopically relevant. The idea of gauge invariance provides a powerful tool to establish the interface as an autonomous thermodynamic subsystem and, thus, to clarify the subtle role of "local equilibrium" in the presence of interfaces.

From a theoretical point of view, it would be desirable to develop a deeper understanding of the moving interface normal transfer term. Like the Poisson bracket itself, it should result from the properties of the group of space transformations and its action on other fields but for a partitioned space. In addition, there might be a deep connection between this term and the idea of gauge invariance.

We have developed the general ideas in the context of a two-phase system consisting of a gas and a liquid in which the gas can be dissolved. As a concrete example, we have discussed the growth and collapse of spherical gas bubbles in supersaturated and undersaturated liquids, respectively. At early times, there can be significant differences between the chemical potentials of the gas and the solute. As a consequence, nonequilibrium effects impede bubble growth and collapse; bubble growth is retarded, and the lifetime of collapsing bubbles can increase dramatically.

The formulation of boundary conditions for the thermally induced growth of vapor bubbles in liquids has been examined previously [33–35]. In some cases, the assumption of a thermodynamic equilibrium at the interface has been relaxed using the framework of linear irreversible thermodynamics [33,34]. It is of interest to note that similar to the results shown in this work, it has been found that nonequilibrium effects at the interface lead to a reduction in bubble growth rates [33].

ACKNOWLEDGMENTS

Helpful discussions with Manuel Laso and Leonard Sagis on conceptual issues of nonequilibrium thermodynamics with moving interfaces are gratefully acknowledged. The authors thank Markus Hütter for many constructive comments on a first draft of this paper.

---

[1] J. W. Gibbs, *Thermodynamics*, The Scientific Papers of J. Willard Gibbs Vol. 1 (Ox Bow, Woodbridge, 1993).
[2] L. Waldmann, Z. Naturforsch. A **22**, 1269 (1967).
[3] D. Bedeaux, A. M. Albano, and P. Mazur, Physica A **82**, 438 (1976).
[4] D. Bedeaux, Adv. Chem. Phys. **64**, 47 (1986).
[5] A. M. Albano and D. Bedeaux, Physica A **147**, 407 (1987).
[6] M. Grmela and H. C. Öttinger, Phys. Rev. E **56**, 6620 (1997).
[7] H. C. Öttinger and M. Grmela, Phys. Rev. E **56**, 6633 (1997).
[8] H. C. Öttinger, *Beyond Equilibrium Thermodynamics* (Wiley, Hoboken, 2005).
[9] H. C. Öttinger, Phys. Rev. E **73**, 036126 (2006).
[10] H. C. Öttinger, J. Non-Newtonian Fluid Mech. **152**, 66 (2008).
[11] A. N. Beris and H. C. Öttinger, J. Non-Newtonian Fluid Mech. **152**, 2 (2008).
[12] A. A. Proussevitch and D. L. Sahagian, J. Geophys. Res. **101**, 17447 (1996).
[13] R. S. Srinivasan, W. A. Gerth, and M. P. Powell, J. Appl. Physiol. **86**, 732 (1999).
[14] R. J. Koopmans, J. C. F. den Doelder, and A. Paquet, Adv. Mater. **12**, 1873 (2000).
[15] J. L. Duda and J. S. Vrentas, AIChE J. **15**, 351 (1969).
[16] J. L. Duda and J. S. Vrentas, Int. J. Heat Mass Transfer **14**, 395 (1971).
[17] L. E. Scriven, Chem. Eng. Sci. **10**, 1 (1959).
[18] E. J. Barlow and W. E. Langlois, IBM J. Res. Dev. **6**, 329 (1962).
[19] E. Zana and L. G. Leal, Ind. Eng. Chem. Fundam. **14**, 175 (1975).
[20] D. C. Venerus and N. Yala, AIChE J. **43**, 2948 (1997).
[21] D. C. Venerus, N. Yala, and B. Bernstein, J. Non-Newtonian Fluid Mech. **75**, 55 (1998).
[22] J. C. Slattery, L. Sagis, and E.-S. Oh, *Interfacial Transport Phenomena*, 2nd ed. (Springer, New York, 2007).

[23] D. A. Edwards, H. Brenner, and D. T. Wasan, *Interfacial Transport Processes and Rheology, Butterworth-Heinemann Series in Chemical Engineering* (Butterworth-Heinemann, Boston, 1991).

[24] H. C. Öttinger, J. Chem. Phys. **130**, 114904 (2009).

[25] A. M. Albano, D. Bedeaux, and J. Vlieger, Physica A **99**, 293 (1979).

[26] E. Johannessen and D. Bedeaux, Physica A **330**, 354 (2003).

[27] K. S. Glavatskiy and D. Bedeaux, Phys. Rev. E **79**, 031608 (2009).

[28] A. N. Beris and B. J. Edwards, *The Thermodynamics of Flowing Systems* (Oxford University Press, New York, 1994).

[29] H. C. Öttinger, Phys. Rev. Lett. **99**, 130602 (2007).

[30] G. L. Pollack, Rev. Mod. Phys. **41**, 48 (1969).

[31] I. M. Gelfand and S. V. Fomin, *Calculus of Variations* (Prentice-Hall, Englewood Cliffs, NJ, 1963).

[32] M. Caracotsios and W. E. Stewart, Comput. Chem. Eng. **9**, 359 (1985).

[33] W. J. Bornhorst and G. N. Hatsopoulos, J. Appl. Mech. **34**, 847 (1967).

[34] H. Wiechert, J. Phys. C **9**, 553 (1976).

[35] A. Prosperetti, Meccanica **14**, 34 (1979).