On the Gibbs–Duhem Relation for Phase-Field Models of Polymeric Mixtures

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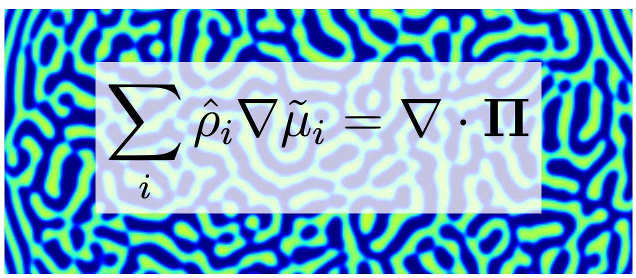

Abstract

Phase-field models are relatively inexpensive field-based models capable of capturing non-equilibrium multiphase behavior of polymers and other soft materials. With their rise in popularity over the past several years, questions have arisen concerning the thermodynamic consistency of some model formulations. In doing so, researchers have employed several different forms of the Gibbs–Duhem equation—a classical thermodynamic relationship used to assess consistency—leading to questions about the correct form of this expression for inhomogeneous mixtures. In this paper, we derive a generalized Gibbs–Duhem relation that is valid for phase-field models. The key to the derivation is the recognition that the functional derivatives used with phase-field models give exchange chemical potentials, in contrast to the classical chemical potentials

commonly used in homogeneous thermodynamics. We use this derivation to demonstrate that a phase-field model that generalizes the Flory–Huggins model satisfies the Gibbs–Duhem expression and is therefore thermodynamically consistent. Additionally, we find that the Gibbs–Duhem relationship provides some unique insights into the relationship between the traditional chemical potentials, the exchange chemical potentials, and the osmotic stress tensor.

Introduction

Phase-field models have been increasingly used in the last two decades in simulations of polymers and soft materials for describing multiphase systems undergoing phase separation, mass transfer, and fluid flow.[1–6] For example, researchers have demonstrated their utility in simulating the formation of polymer membranes including the processes of phase separation, microstructural evolution, and kinetic arrest in a complex multicomponent polymer solution.[3,7] Recently, several authors have begun probing the thermodynamic consistency of a variety of phase-field models, with a focus on whether or not they obey the Gibbs–Duhem equation.[4,8] The Gibbs–Duhem equation is a classical relationship for assessing thermodynamic consistency in mixture thermodynamics[9,10]

$$\sum_i n_i \, d\mu_i = -S \, dT + V \, dP \tag{1}$$

where n_i is the number of molecules of component i, μ_i is the chemical potential, S is the entropy, T is the temperature, V is the system volume, and P is the system pressure. In this paper, we attempt to resolve the ongoing confusion about the Gibbs–Duhem equation by obtaining its correct form for phase-field models. We then use our expression to demonstrate the thermodynamic consistency of a popular phase-field model used for polymer solutions and blends.

Phase-field models differ from classical thermodynamics by permitting inhomogeneous fields of concentration, pressure, temperature, etc.[11] The presence of these inhomogeneities necessitates a generalization of the free energy, and for a phase-field model of a mixture of fluids the Helmholtz energy

$$F[\hat{\rho}_1, \hat{\rho}_2, \cdots] = \int d\boldsymbol{r} \Big[f_0(\hat{\rho}_1, \hat{\rho}_2, \cdots) + g(\nabla\hat{\rho}_1, \nabla\hat{\rho}_2, \cdots) \Big] \tag{2}$$

is a functional of z number density fields $\hat{\rho}_i = \hat{\rho}_i(\boldsymbol{r})$ of the species of the mixture. In Eq. 2, f_0 is a homogeneous intensive mixing free energy density, and g is a free energy density describing interfacial energies. An exchange chemical potential (also called a diffusional potential)[8,12–15] can be defined for the system by taking the functional derivative of the free energy functional in Eq. 2

$$\tilde{\mu}_i = \frac{\delta F}{\delta \hat{\rho}_i} = \frac{\partial f_0}{\partial \hat{\rho}_i} - \nabla \cdot \frac{\partial g}{\partial \nabla \hat{\rho}_i} \tag{3}$$

As we will see, the use of this definition leads to subtle consequences for the final form of the Gibbs-Duhem relationship for phase-field models.

The literature contains different versions of the Gibbs–Duhem relationship for phase-field models, and these approaches can be sub-divided into two categories. First, numerous researchers have used mechanical equilibrium arguments to derive an expression for the osmotic stress of a single-component, two-phase system.[8,14,16–21] This approach begins with a momentum balance

$$\rho \left(\frac{\partial v}{\partial t} + \boldsymbol{v} \cdot \nabla \boldsymbol{v} \right) = -\nabla \cdot \boldsymbol{\sigma} + \rho \nabla U_{ext} \tag{4}$$

where ρ is the total mass density, v is the velocity, t is the time, $\boldsymbol{\sigma}$ is the total stress tensor, and U_{ext} is an external potential. In steady state conditions, Eq. 4 simplifies to[17]

$$\rho \nabla U_{\text{ext}} = \nabla \cdot \boldsymbol{\sigma} \tag{5}$$

Assuming that the osmotic stress, $\boldsymbol{\Pi}$, and the exchange chemical potential, $\tilde{\mu}$, can replace $\boldsymbol{\sigma}$

and U_{ext} respectively, one obtains

$$\hat{\rho}\nabla\tilde{\mu} = \nabla \cdot \mathbf{\Pi} \tag{6}$$

in the absence of fluid velocities. For a steady-state multicomponent mixture, one assumes that the left hand side of Eq. 5 consists of a linear combination of exchange chemical potentials,[18,22] resulting in

$$\sum_{i=1}^{z-1} \hat{\rho}_i \nabla\tilde{\mu}_i = \nabla \cdot \mathbf{\Pi} \tag{7}$$

Liu *et al.*[14] has claimed that Eq. 7 is a valid expression of the Gibbs–Duhem relation for multicomponent phase-field models.

The second approach uses the homogeneous Gibbs–Duhem relation in Eq. 1 from classical thermodynamics as a starting point.[4,23] In contrast to arguments based on mechanical equilibrium, researchers using the thermodynamic approach rely on the traditional chemical potential and state the Gibbs–Duhem relationship as[4,23,24]

$$\sum_{i=1}^{z} \hat{\rho}_i \nabla\mu_i = 0 \tag{8}$$

when temperatures and pressures are constant. There has been some confusion in this literature over the use of traditional and exchange chemical potentials in Eq. 8, leading to yet another possible version

$$\sum_{i=1}^{z} \hat{\rho}_i \nabla\tilde{\mu}_i = 0 \tag{9}$$

We seek to reconcile these approaches and provide a definitive answer to the question of the correct Gibbs–Duhem relation for multicomponent phase-field models. In doing so, we will need to resolve the apparent conflict between the use of the traditional and exchange chemical potentials in the above expressions. Additionally, by providing a rigorous derivation of the correct expression, we aim to resolve an ongoing controversy surrounding claims[4] that several popular phase-field models—including the Cahn–Hilliard model[6,11] and a multicomponent Flory–Huggins–de Gennes model[12,19,25]—do not satisfy Gibbs–Duhem and are therefore thermodynamically inconsistent.

Consequently, in this work we build upon prior literature to provide a transparent and consistent theoretical framework spanning both homogeneous thermodynamics and inhomogeneous phase-field models that leads to expressions for the Gibbs–Duhem relationship. We first provide a rigorous derivation of the Gibbs–Duhem relationship for a homogeneous, multicomponent system using principles from classical thermodynamics. This derivation provides key insights into the relationship between the classical chemical potential, exchange chemical potential, and the osmotic stress. In the following section, we extend our derivation and postulate a Gibbs–Duhem relationship for an inhomogeneous system. We find that *Eq. 7 and Eq. 8 are equivalent and valid expressions of the Gibbs–Duhem relationship*, thereby resolving the apparent controversy in the literature. However, we also find that the traditional chemical potential in Eq. 8 is inconvenient to use for phase-field models, and therefore Eq. 7 is preferred. Finally, we conclude with a concrete example, demonstrating the thermodynamic consistency of a multicomponent Flory–Huggins–de Gennes model that we and others have used in several studies.[1,3,7,12,26]

Gibbs–Duhem Relation for a Homogeneous System

In this section, we use principles of classical thermodynamics to derive the Gibbs–Duhem equation in terms of exchange chemical potentials. As outlined above, we suspect that much of the confusion on this topic originates from a misunderstanding of the relationship between traditional chemical potentials and exchange chemical potentials. As such, we are careful to explicitly define both here.

The traditional chemical potential is defined as

$$\mu_i = \left(\frac{\partial F_0}{\partial n_i}\right)_{T,V,n_{j\neq i}} \tag{10}$$

where $F_0 = f_0 V$ is the extensive (Helmholtz) free energy of a homogeneous multicomponent system, and n_i is the number of molecules of component i. As expressed by the fundamental relation of thermodynamics,[9,10]

$$dF_0 = SdT - PdV + \sum_{i=1}^{z} \mu_i dn_i \tag{11}$$

the constant temperature and volume thermodynamic phase behavior of the system is completely determined by the chemical potentials: $\mu_1, \mu_2, \ldots, \mu_z$. The Gibbs–Duhem relation for a compressible, multicomponent system is given by Eq. 1, and for an incompressible liquid-liquid phase separation commonly considered in systems of soft materials,[4,12] temperature and pressure are constant, simplifying the relation to

$$\sum_{i=1}^{z} n_i d\mu_i = 0. \tag{12}$$

An alternate, but equally valid set of thermodynamic potentials can be used in addition to the traditional chemical potential in Eq. 10. These are the so-called "exchange" chemical potentials and the osmotic pressure, which are defined respectively as,

$$\tilde{\mu}_i = \frac{1}{V}\left(\frac{\partial F_0}{\partial \hat{\rho}_i}\right)_{T,V,\hat{\rho}_{j\neq i},m} = \left(\frac{\partial f_0}{\partial \hat{\rho}_i}\right)_{T,V,\hat{\rho}_{j\neq i},m} \tag{13}$$

$$\pi = -\left(\frac{\partial F_0}{\partial V}\right)_{T,\hat{V},w_i} \tag{14}$$

Note that Eq. 14 is defined at constant specific volume but variable mass, making it an osmotic pressure (as we describe in more detail below). For the homogeneous case, it is convenient to use a mass fraction, w_i, instead of the number density as the former is more commonly encountered in homogeneous thermodynamics. The two concentrations are closely related. The mass fraction is given by

$$w_i = \frac{n_i M_i}{m} \tag{15}$$

where M_i is the molecular weight of component i, and m is the total system mass. The number density is given by

$$\hat{\rho}_i = \frac{n_i N_i}{V} \tag{16}$$

where N_i is the degree of polymerization. Using the fact that $N_i = M_i/M_i^0$, where M_i^0 the molecular weight of a monomer of component i, one can relate the two concentrations using

$$w_i = \hat{\rho}_i M_i^0 \hat{V} \tag{17}$$

with $\hat{V}$ giving the specific volume of the mixture. Substituting the latter into Eq. 13 gives

$$\tilde{\mu}_i = \frac{M_i^0}{m} \left(\frac{\partial F_0}{\partial w_i}\right)_{T,V,w_{j\neq i},m} = M_i^0 \ \hat{V} \left(\frac{\partial f_0}{\partial w_i}\right)_{T,V,w_{j\neq i},m} \tag{18}$$

To obtain the Gibbs–Duhem equation for a compressible multicomponent system, we first re-express the total derivative of the homogeneous free energy as a function of the independent mass fractions w_i and the total system mass m,[9,10]

$$dF_0 = S \ dT - P \ dV + \sum_{i=1}^{z-1} \left(\frac{\partial F_0}{\partial w_i}\right)_{T,V,w_{j\neq i},m} dw_i + \left(\frac{\partial F_0}{\partial m}\right)_{T,V,w_i} dm \tag{19}$$

instead of n_i.

It is convenient to manipulate Eq. 19 so that F_0 depends on only one extensive quantity: the total mass. Accordingly, we substitute the definition of the specific volume $V = m\hat{V}$ into Eq. 19, and expand the derivatives and collect like terms to give

$$dF_0 = SdT - mPd\hat{V} + \sum_{i=1}^{z-1} \left(\frac{\partial F_0}{\partial w_i}\right)_{T,V,w_{j\neq i},m} dw_i + \left[\left(\frac{\partial F_0}{\partial m}\right)_{T,V,w_i} - P\hat{V}\right] dm \tag{20}$$

Additional insight into the meaning of the terms in Eq. 20 can be obtained by comparing them to the total derivative of the homogeneous free energy

$$dF_0 = \left(\frac{\partial F_0}{\partial T}\right)_{\hat{V},w_i,m} dT + \left(\frac{\partial F_0}{\partial \hat{V}}\right)_{T,w_i,m} d\hat{V} + \sum_{i=1}^{z-1} \left(\frac{\partial F_0}{\partial w_i}\right)_{T,\hat{V},w_{j\neq i},m} dw_i + \left(\frac{\partial F_0}{\partial m}\right)_{T,\hat{V},w_i} dm \tag{21}$$

whose independent variables are T, $\hat{V}$, w_i, and m. As expected, the first term identifies the entropy as

$$S = \left(\frac{\partial F_0}{\partial T}\right)_{\hat{V},w_i,m} \tag{22}$$

and the second term identifies the traditional definition of the pressure

$$P = -\frac{1}{m}\left(\frac{\partial F_0}{\partial \hat{V}}\right)_{T,w_i,m} = -\left(\frac{\partial F_0}{\partial V}\right)_{T,w_i,m} \tag{23}$$

The third term identifies the exchange chemical potential

$$\tilde{\mu}_i = \frac{M_i^0}{m}\left(\frac{\partial F_0}{\partial w_i}\right)_{T,V,w_{j\neq i},m} \tag{24}$$

noting that the constraint of constant specific volume and constant mass is equivalent to one of constant volume. The fourth term provides an expression for the osmotic pressure

$$\pi = -\frac{1}{\hat{V}}\left(\frac{\partial F_0}{\partial m}\right)_{T,\hat{V},w_i} = -\left(\frac{\partial F_0}{\partial V}\right)_{T,\hat{V},w_i} \tag{25}$$

$$= P - \frac{1}{\hat{V}}\left(\frac{\partial F_0}{\partial m}\right)_{T,V,w_i} \tag{26}$$

as the change in free energy with a change in total volume at constant composition and specific volume. Note the meaningful difference between the definition of the thermodynamic pressure and the osmotic pressure, with the former being held at constant mass (and variable specific volume) and the latter at constant specific volume (and variable mass). Finally, substituting Equations 22–25 into Eq. 21 gives

$$dF_0 = SdT - mPd\hat{V} + \sum_{i=1}^{z-1} \frac{m\tilde{\mu}_i}{M_i^0} dw_i - \pi\hat{V}dm \tag{27}$$

To obtain a Gibbs–Duhem expression, we follow the traditional approach using Euler's theorem,[9,10] and integrate Eq. 27 to give the free energy

$$F_0 = \sum_{i=1}^{z-1} \frac{m\tilde{\mu}_i w_i}{M_i^0} - \pi\hat{V}m \tag{28}$$

Next, we take the total derivative of Eq. 28

$$dF_0 = \sum_{i=1}^{z-1} \left[(\frac{m\tilde{\mu}_i}{M_i^0})dw_i + w_i d(\frac{m\tilde{\mu}_i}{M_i^0}) \right] - (\pi\hat{V})dm - md(\pi\hat{V}) \tag{29}$$

and subtract it from Eq. 27. Expanding the derivatives and collecting like terms gives

$$0 = -SdT + m(P - \pi)d\hat{V} + \sum_{i=1}^{z-1} \frac{w_i}{M_i^0} d(m\tilde{\mu}_i) - Vd\pi \tag{30}$$

which is an expression of the Gibbs–Duhem relationship for a homogeneous systems in terms of the exchange chemical potential and osmotic presure. Keep in mind that up to this point, the system has been compressible and nonisothermal, however, in liquid-liquid phase separation we frequently assume an incompressible and isothermal system. Assuming incompressibility, i.e. that $\hat{V}$ and T are constant, simplifies Eq. 30 to

$$\sum_{i=1}^{z-1} \hat{\rho}_i d\tilde{\mu}_i = d\pi \tag{31}$$

Note also that the pressure becomes ill-defined for an incompressible system, as is well-known for example in the study of fluid mechanics.[27] The pressure is conjugate to the specific volume and therefore does not appear in Eq. 31, however, one must use caution when employing the preceeding equations for an incompressible system.

The above analysis demonstrates that the combination of the exchange chemical potentials and osmotic pressure are thermodynamically equivalent to the traditional chemical potentials. Consequently, Equations 30 and 31 are the analogue of the Gibbs–Duhem relationships in Equations 1 and 12 respectively. We provide further evidence that these approaches are interchangeable by producing mathematical relations between the exchange chemical potentials, osmotic pressure, and the traditional chemical potentials. Based on our experience, the following relationships are not easily found in the literature, and they provide a useful way to convert between the two approaches. For simplicity in deriving these relationships, we assume that the system is incompressible, i.e. that $\hat{V}$ is a constant.

Using a chain rule, we expand the definition of the exchange chemical potential from Eq. 24

$$\tilde{\mu}_i = \frac{M_i^0}{m}\left(\frac{\partial F_0}{\partial w_i}\right)_{T,V,w_{j\neq i},m} \tag{32}$$

$$= \frac{M_i^0}{m}\sum_{j=1}^{z}\left(\frac{\partial F_0}{\partial n_i}\right)_{T,V,w_{i\neq j},m}\left(\frac{\partial n_i}{\partial w_j}\right)_{T,V,w_{i\neq j},m} \tag{33}$$

Evaluating the second term on the right-hand side gives[9]

$$\left(\frac{\partial n_i}{\partial w_j}\right)_{T,V,w_{i\neq j},m} = c_{ij}\,\frac{m}{M_i} \tag{34}$$

where the constant c_{ij} is given by

$$c_{ij} = \begin{Bmatrix} 1, & \text{if } i = j \\ 0, & \text{if } i \neq j \\ -1, & \text{if } i = z \end{Bmatrix} \tag{35}$$

Substituting the definition of the chemical potential from Eq. 10 and simplifying gives

$$\tilde{\mu}_i = M_i^0\left[\frac{\mu_i}{M_i} - \frac{\mu_z}{M_z}\right]. \tag{36}$$

An explicit expression for π can be found by substituting Eq. 36 into the simplified Gibbs–Duhem expression in Eq. 31 giving

$$d\pi = \sum_{i=1}^{z-1} \hat{\rho}_i \; d\left(M_i^0 \left[\frac{\mu_i}{M_i} - \frac{\mu_z}{M_z} \right] \right) \tag{37}$$

$$= \left[\frac{\hat{\rho}_1}{N_1} d\mu_1 + \frac{\hat{\rho}_2}{N_2} d\mu_2 + ... - (\frac{m}{VM_z} - \frac{\hat{\rho}_z}{N_z}) d\mu_z \right] \tag{38}$$

Simplifying the above using Eq. 12 and integrating gives an explicit expression for the osmotic pressure,

$$\pi = -\frac{m}{VM_z}\mu_z \tag{39}$$

At least for an incompressible system, the relationships between the two types of chemical potentials are simple and straightforward to interpret. Exchange chemical potentials are *relative* to a reference chemical potential μ_z, and the osmotic pressure is proportional to this reference. Additionally, one notes that in contrast to the traditional chemical potentials, the osmotic pressure has units of a pressure. The appearance of the z^{th}-component in Eq. 36 and Eq. 39 is also curious, given that the choice of the z is arbitrary. This peculiarity is a consequence of incompressibility and the fact that the z^{th} component is not an independent variable. Consequently, for an incompressible system one can think of the z^{th} component as the implicit "osmotic medium" in which diffusion takes place.

Gibbs–Duhem Relation for an Inhomogeneous System

With the above thermodynamic relationships in mind, we now turn our attention to inhomogeneous models which employ free energy functionals rather than free energy functions, necessitating a further generalization to the Gibbs–Duhem relationship in Eq. 31. Based on a straightforward generalization of the homogeneous relationship in Eq. 31, one can generalize the Gibbs–Duhem relationship for an inhomogeneous, incompressible, and isothermal system,

$$\sum_{i=1}^{z-1} \hat{\rho}_i \nabla \tilde{\mu}_i = \nabla \cdot \mathbf{\Pi} \tag{40}$$

where $\mathbf{\Pi}$ is the second-rank osmotic stress tensor and $\tilde{\mu}_i$ is the exchange chemical potential for component i. We seek to justify Eq. 40 more rigorously.

A chemical potential can be rigorously defined for an inhomogeneous system by taking a Legendre transform of Eq. 2 to obtain the grand potential[20,28]

$$\Omega[\{\hat{\rho}_i\}] = F[\{\hat{\rho}_i\}] - \sum_i \tilde{\mu}_i \int d\boldsymbol{r} \hat{\rho}_i(\boldsymbol{r}) \tag{41}$$

The grand potential obeys the variational principle $\delta\Omega = 0$, and taking the functional derivative

$$\frac{\delta \Omega}{\delta \hat{\rho}_i} = \frac{\delta F}{\delta \hat{\rho}_i} - \tilde{\mu}_i = 0 \tag{42}$$

identifies $\delta F/\delta\hat{\rho}_i$ as the local exchange chemical potential of i at $\boldsymbol{r}$ conjugate to $\hat{\rho}_i$ as originally expressed in Eq. 3. We suppose that one may also attempt to formally express a traditional chemical potential using the functional derivative[23]

$$\mu_i = \frac{\delta F}{\delta n_i} \tag{43}$$

but the evaluation of such an expression is not straightforward since n_i is an extensive quantity that is itself a functional of $\hat{\rho}_i$. Consequently, Eq. 3 is overwhelmingly preferred in the literature.[14,18,20,21,29]

With a firm definition of the exchange chemical potential, we derive the inhomogeneous Gibbs–Duhem relation for multicomponent systems. The rate of work done by osmotic forces (per unit volume), $\boldsymbol{h}_i$, in the system is given by

$$\frac{\partial F}{\partial t} = \int d\boldsymbol{r} \left[\sum_{i=1}^{z-1} \boldsymbol{h}_i \cdot \boldsymbol{v}_i \right] \tag{44}$$

We seek to manipulate the free energy functional in Eq. 2 to this form. Taking the time derivative of $F[\{\hat{\rho}_i\}]$ and using the chain rule gives,

$$\frac{\partial F}{\partial t} = \int d\boldsymbol{r} \left[\sum_{i=1}^{z-1} \frac{\delta F}{\delta \hat{\rho}_i} \frac{\partial \hat{\rho}_i}{\partial t} \right] \tag{45}$$

$$= \int d\boldsymbol{r} \left[\sum_{i=1}^{z-1} \tilde{\mu}_i \frac{\partial \hat{\rho}_i}{\partial t} \right]. \tag{46}$$

The species mass conservation equation for component i is given by

$$\frac{\partial \hat{\rho}_i}{\partial t} = -\nabla \cdot (\hat{\rho}_i \boldsymbol{v}_i) \tag{47}$$

where $\boldsymbol{v}_i$ is the velocity of component i. Substituting Eq. 47 into Eq. 46 and using the product rule

$$\nabla \cdot (\tilde{\mu}_i \hat{\rho}_i \boldsymbol{v}_i) = \tilde{\mu}_i \nabla \cdot (\hat{\rho}_i \boldsymbol{v}_i) + \hat{\rho}_i \nabla \tilde{\mu}_i \cdot \boldsymbol{v}_i \tag{48}$$

to perform integration by parts gives

$$\frac{\partial F}{\partial t} = -\int d\boldsymbol{r} \big[\sum_{i=1}^{z-1} \nabla \cdot (\tilde{\mu}_i \hat{\rho}_i \boldsymbol{v}_i) - \hat{\rho}_i \nabla \tilde{\mu}_i \cdot \boldsymbol{v}_i \big] \tag{49}$$

$$= \int d\boldsymbol{r} \big[\sum_{i=1}^{z-1} \hat{\rho}_i \nabla \tilde{\mu}_i \cdot \boldsymbol{v}_i \big] \tag{50}$$

Note that the first term in the summation in Eq. 49 is zero through the use of Gauss' divergence theorem and natural boundary conditions. Eq. 50 identifies the osmotic forces (in a medium of component z) as $\boldsymbol{h}_i = \hat{\rho}_i \nabla \tilde{\mu}_i$. Consequently, using the conventional relation between stresses and forces,[30] the divergence of the osmotic stress is given by

$$\nabla \cdot \boldsymbol{\Pi} = \sum_{i=1}^{z-1} \boldsymbol{h}_i \tag{51}$$

giving the Gibbs–Duhem relationship in Eq. 40.

Having specified the form of the free energy functional, it is also possible to provide an explicit expression for $\mathbf{\Pi}$. We obtain it by first taking the gradient of the free energy density in Eq. 2

$$\nabla\Big[f_0(\hat{\rho}_1, \hat{\rho}_2, ...) + g(\nabla\hat{\rho}_1, \nabla\hat{\rho}_2, ...)\Big] = \sum_{i=1}^{z-1}\left(\frac{\partial f_0}{\partial\hat{\rho}_i}\nabla\hat{\rho}_i + \frac{\partial g}{\partial\nabla\hat{\rho}_i}\cdot\nabla\nabla\hat{\rho}_i\right) \tag{52}$$

Using Eq. 3 to replace the partial derivatives of f_0, empolying the product rule from vector calculus $\nabla(\tilde{\mu}_i\hat{\rho}_i) = \tilde{\mu}_i\nabla\hat{\rho}_i + \hat{\rho}_i\nabla\tilde{\mu}_i$, and noting that $\nabla\psi = \nabla\cdot(\psi\boldsymbol{I})$, one finally obtains

$$\sum_{i=1}^{z-1}\hat{\rho}_i\nabla\tilde{\mu}_i = \nabla\cdot\left[\left((\sum_{i=1}^{z-1}\hat{\rho}_i\tilde{\mu}_i) - f_0 - g\right)\boldsymbol{I} + \sum_{i=1}^{z-1}\frac{\partial g}{\partial\nabla\hat{\rho}_i}\nabla\hat{\rho}_i\right] \tag{53}$$

after considerable algebraic manipulation. The osmotic stress tensor is therefore given by

$$\mathbf{\Pi} = \left((\sum_{i=1}^{z-1}\hat{\rho}_i\tilde{\mu}_i) - f_0 - g\right)\boldsymbol{I} + \sum_{i=1}^{z-1}\frac{\partial g}{\partial\nabla\hat{\rho}_i}\nabla\hat{\rho}_i \tag{54}$$

where $\boldsymbol{I}$ is the identity matrix. As a further proof of consistency, when $z = 2$ Eq. 54 reduces to the binary stress tensor obtained by Dean et. al.[31]

Thermodynamic Consistency of a Multicomponent Flory–Huggins–de Gennes Model

Flory–Huggins theory is a classical cornerstone for describing the thermodynamics and phase-behavior of polymeric solutions and blends. De Gennes expanded the theory for inhomogeneous mixtures using the so-called random phase approximation leading to the inclusion of square gradient terms (i.e. $|\nabla\phi|^2$) that penalize composition fluctuations.[32,33] In our present formalism, a multicomponent Flory–Huggins–de Gennes model can be specified by defining the local free energy

$$f_0(\{\phi_i\}) = \sum_{i=1}^{z}\frac{\phi_i}{N_i}\ln\phi_i + \sum_{i=1}^{z}\sum_{j<i}\chi_{ij}\phi_i\phi_j \tag{55}$$

and gradient terms

$$g(\{\nabla\phi_i\}) = \frac{1}{2}\sum_{i=1}^{z} \kappa_i \left|\nabla\phi_i\right|^2 \tag{56}$$

in the free energy functional in Eq. 2. In the above, N_i is the degree of polymerization of component i, χ_{ij} is the binary interaction parameter between components i and j, and κ_i are phenomenological gradient coefficients penalizing interfaces. De Gennes obtained functional forms for the composition dependence of κ_i, but as is often the case in the literature, we assume here that they are constants.

Notably, in these Flory–Huggins-type models, one typically employs the volume fraction of component i, ϕ_i rather than the number density. The volume fraction is given by

$$\phi_i = \frac{n_i N_i \mathrm{v}_i^0}{V} = \hat{\rho}_i \mathrm{v}_i^0 \tag{57}$$

where v_i^0 is the volume of monomer i. Keeping with the spirit of the original lattice models v_i^0 is typically assumed to be a constant v^0, as is the monomer mass, $M_i^0 = M^0$, rendering the system incompressible with a specific volume $\hat{V} = \mathrm{v}^0/M^0$. With these assumptions, mass fractions are equivalent to volume fractions, $w_i = \phi_i$, and incompressibility ensures that $\phi_z = 1 - \sum_{i=1}^{z-1} \phi_i$.

Accordingly, the inhomogeneous Gibbs–Duhem relationship simplifies to

$$\sum_{i=1}^{z-1} \phi_i \nabla\tilde{\mu}_i = \mathrm{v}^0 \left(\nabla \cdot \mathbf{\Pi}\right) \tag{58}$$

To verify that the Flory–Huggins–de Gennes model is thermodynamically consistent it is sufficient to show that this equality holds. The osmotic stress on the right-hand side is obtained from Eq. 54 and is given by

$$\mathrm{v}^0\,\mathbf{\Pi} = \left[\sum_{i=1}^{z-1} \phi_i \frac{\partial f_0}{\partial \phi_i} - \sum_{i=1}^{z-1}\sum_{j=1}^{z-1} \phi_i K_{ij} \nabla^2 \phi_j - f_0 - g\right] \boldsymbol{I} + \sum_{i=1}^{z-1}\sum_{j=1}^{z-1} K_{ij}^T \nabla\phi_i \nabla\phi_j \tag{59}$$

In the above, it is convenient to rewrite Eq. 56 as

$$g = \frac{1}{2}\sum_{i=1}^{z-1}\sum_{j=1}^{z-1} K_{ij}\left(\nabla\phi_i \cdot \nabla\phi_j\right) \tag{60}$$

where the matrix K_{ij} is a symmetric matrix of the κ_i

$$K_{ij} = \begin{cases} \kappa_i + \kappa_z, & \text{if } i = j \\ \kappa_z, & \text{if } i \neq j \end{cases} \tag{61}$$

This osmotic stress is consistent with those given by others for single component Flory–Huggins–de Gennes models.[34,35] Taking the divergence of the osmotic stress in Eq. 59 gives

$$\begin{aligned} \mathrm{v}^0\left(\nabla\cdot\mathbf{\Pi}\right) = &\sum_{i=1}^{z-1}\left[\phi_i\nabla\frac{\partial f_0}{\partial\phi_i} + \frac{\partial f_0}{\partial\phi_i}\nabla\phi_i\right] - \left[\sum_{i=1}^{z-1}\sum_{j=1}^{z-1} K_{ij}(\phi_i\nabla\nabla^2\phi_j + \nabla^2\phi_j\nabla\phi_i)\right] \\ &- \nabla f_0 - \nabla g + \sum_{i=1}^{z-1}\sum_{j=1}^{z-1} K_{ij}\nabla^2\phi_i\nabla\phi_j \end{aligned} \tag{62}$$

and using the product rule and simplifying leads to,

$$\mathrm{v}^0\left(\nabla\cdot\mathbf{\Pi}\right) = \sum_{i=1}^{z-1}\phi_i\nabla\frac{\partial f_0}{\partial\phi_i} - \sum_{i=1}^{z-1}\sum_{j=1}^{z-1} K_{ij}\phi_i\nabla\nabla^2\phi_j \tag{63}$$

On the left-hand side of Eq. 58, the exchange chemical potential is evaulated by performing the functional derivative in Eq. 3 giving,

$$\tilde{\mu}_i = \frac{\partial f_0}{\partial\phi_i} - \sum_{j=1}^{z-1} K_{ij}\nabla^2\phi_j \tag{64}$$

Substituting this expression into the left-hand side of Eq. 58 yields,

$$\sum_{i=1}^{z-1}\phi_i\nabla\tilde{\mu}_i = \sum_{i=1}^{z-1}\left[\phi_i\nabla\frac{\partial f_0}{\partial\phi_i} - \sum_{j=1}^{z-1}\phi_i K_{ij}\nabla\nabla^2\phi_j\right] \tag{65}$$

which agrees with Eq. 63, completing the proof of consistency.

Discussion and Conclusion

The literature contains at least three competing versions of the Gibbs–Duhem relationship for inhomogeneous multicomponent systems: Equations 7, 8, and 9. The former owes its potential validity to arguments based on the mechanical equilibrium of a single component two-phase system, and the latter two were justified based on homogeneous thermodynamics.

Using purely thermodynamic arguments, we first derived a Gibbs–Duhem relationship for a *homogeneous system* using an exchange chemical potential. This derivation enables two important conclusions. First, the homogeneous version of Eq. 8 (i.e. Eq. 12) using traditional chemical potentials *is not equivalent* to the homogeneous version of Eq. 9, (i.e. $\sum_{i=1}^{z-1} n_i \, d\tilde{\mu}_i = 0$). Accordingly, the latter is not a valid statement of the Gibbs–Duhem relationship. We suspect that the confusion between these two equations originates from a misunderstaning of the difference between traditional chemical potentials and exchange chemical potentials. Second, we showed that a form of the Gibbs-Duhem equation that uses exchange chemical potentials, Eq. 31, *is equivalent* to Eq. 12, showing that an approach using either traditional chemical potentials or exchange chemical potentials can yield a valid Gibbs–Duhem relationship. This derivation also provided additional insight into the physical meaning of the exchange chemical potentials and the osmotic pressure.

Additionally, we demonstrated that exchange chemical potentials are the natural variable for inhomogeneous systems. Because "traditional" chemical potentials are not easily defined for an inhomogeneous system (as is assumed in Eq. 8) a form of Gibbs–Duhem that relies on them is perhaps valid, but it is not easily used. Instead, we used a work-based argument to obtain a general expression for the multicomponent, inhomogeneous Gibbs–Duhem relationship in terms of exchange chemical potentials, and we obtained a general expression for the osmotic stress tensor. This work-based approach is quite similar in spirit to the traditional mechanical equilibrium arguments, and has in fact been used by others for deriving two-fluid models,[19,29,31] though the derivation has not been previously explicitly connected to Gibbs–Duhem.

Taken together, both the homogeneous and inhomogeneous arguments are in agreement, and there is a clear justification that Eq. 7 is a valid and preferred statement of the Gibbs–Duhem relationship for inhomogeneous systems. Importantly, the agreement between the thermodynamic arguments and the work/mechanical arguments in the sections reconcile the apparent disagreement between the two approaches in the literature.

Finally, in the last section, we use our generic formulas to demonstrate the thermodynamic consistency of the popular Flory–Huggins–de Gennes phase-field model.[3,12,19,34,36] This proof is particularly important, because the consistency of these models has been called into question.[4] Indeed, we anticipate that similar disputes will continue to surface as phase-field models increase in both popularity and complexity. Accordingly, we have endeavored to provide clear, generic criteria that can be used to critically examine the thermodynamic consistency of future models.

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