Macromolecules **2002,** *35,* 5331−5333 **5331**

Free Energy Balance for Compression of Polymer Interphases

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Received February 11, 2002
Revised Manuscript Received April 22, 2002

Introduction

An interphase is a three-dimensional region in which material properties vary continuously with position as one passes from one bulk (spatially uniform or homogeneous) phase into another. In this work, our interest centers on polymer−solvent mixtures located in the narrow gap between two impenetrable surfaces. This configuration is an idealization of the interaction between crossed mica cylinders (as found in the surface forces apparatus[1]) or between colloidal spheres for surface−surface separations that are small compared to the objects' radii of curvature. Statistical mechanical models[2] of polymer interphases seek to predict, among other things, the interphase interfacial tension as well as the work required to change the separation of the interphase's bounding surfaces.

In a previous publication,[3] we attempted to construct rigorous mass and energy balances for compression of multicomponent polymer interphases. The derivation presented previously includes an unnecessary incompressibility assumption (ref 3, eq 7) as well as several errors (a statement that constant molar volumes imply incompressibility, sign and notation errors in eqs 14 and 33, and an error in deriving eq 24 making eqs 32 and 33 inconsistent). The previous derivation also employed a confusing mixture of partial mass, partial molar, and partial volume variables. Finally, the decomposition of the stress tensor used previously (eqs 19−22) was obscure and confusing.

A corrected, improved derivation is presented here. The derivation begins with fundamental mass and energy balances using only partial mass variables. The forms of these equations and the transport theorem do not rely on any assumption of incompressibility. The decomposition of the stress tensor is clear and consistent with established forms in continuum mechanics for uniaxial compression. However, the final expressions for interfacial tension and disjoining pressure for compression of polymer interphases remain unchanged and consistent with the findings of earlier work.[3,4]

Generic Free Energy Balance

Correct evaluation of the interfacial tension and work of compression begins with the conservation "laws" from continuum mechanics,[5] including conservation of mass

$$\frac{\mathrm{D}\rho}{\mathrm{D}t} + \rho\nabla\cdot\vec{v} = 0 \tag{1}$$

(ρ and $\vec{v}$ denoting mass density and velocity, $\{\mathrm{D}(\bullet)\}/\{\mathrm{D}t\}$ representing the material derivative[5]), mass of component k

$$\rho\frac{\mathrm{D}\omega_k}{\mathrm{D}t} + \nabla\cdot\vec{j}_k = 0 \tag{2}$$

(ω_k and $\vec{j}_k$ denoting mass fraction and flux for component k), and total energy

$$\rho\frac{\mathrm{D}\left(\hat{U} + \frac{1}{2}v^2\right)}{\mathrm{D}t} = -\nabla\cdot\vec{q} + \nabla\cdot(\mathbf{T}\cdot\vec{v}) \tag{3}$$

(internal energy per unit mass $\hat{U}$, energy flux vector $\vec{q}$, and stress tensor $\mathbf{T}$). Equation 3 neglects body forces, chemical reactions, and radiant energy transmission. The scalar (dot) product of velocity with the differential equation for conservation of linear momentum gives

$$\rho\frac{\mathrm{D}\left(\frac{1}{2}v^2\right)}{\mathrm{D}t} = \nabla\cdot(\mathbf{T}\cdot\vec{v}) - \mathrm{tr}(\mathbf{T}\cdot\nabla\vec{v}) \tag{4}$$

For processes that change the state of the system slowly and reversibly, the entropy inequality (second law of thermodynamics) becomes an equality. We thus have

$$\rho\frac{\mathrm{D}\hat{S}}{\mathrm{D}t} + \frac{1}{T}\nabla\cdot\vec{e} = 0 \tag{5}$$

assuming constant temperature (entropy per unit mass $\hat{S}$; thermal energy flux vector $\vec{e}$).

Subtracting eqs 4 and 5 (the latter multiplied by T) from eq 3 yields a form of the energy balance

$$\rho\frac{\mathrm{D}\hat{A}}{\mathrm{D}t} = -\nabla\cdot(\vec{q} - \vec{e}) + \mathrm{tr}(\mathbf{T}\cdot\nabla\vec{v}) = -\nabla\cdot\Big(\sum_k \mu_k^{\mathrm{m,b}}\vec{j}_k\Big) + \mathrm{tr}(\mathbf{T}\cdot\nabla\vec{v}) \tag{6}$$

in terms of the Helmholtz free energy per unit mass, $\hat{A}$. The second form of eq 6 invokes an established relationship (ref 5, p 449) between energy flux vectors and the mass flux vector. The chemical potential (μ_k^{m}, superscript m denoting mass basis) has the same value at every position (equal to the "bulk" solution value, superscipt b) as a consequence of the "quasi-equilibrium" assumption invoked for eq 5. This and eq 2 lead to

$$\rho\frac{\mathrm{D}\hat{A}}{\mathrm{D}t} = \sum_k \mu_k^{\mathrm{m,b}}\left(\rho\frac{\mathrm{D}\omega_k}{\mathrm{D}t}\right) + \mathrm{tr}(\mathbf{T}\cdot\nabla\vec{v}) \tag{7}$$

Finally, we integrate eq 7 over the entire volume of the system V (interphase plus bulk phases). Application of one form of the transport theorem (ref 5, p 22) produces

$$\frac{\mathrm{d}A}{\mathrm{d}t} = \sum_k \mu_k^{\mathrm{b}}\frac{\mathrm{d}N_k}{\mathrm{d}t} + \int_V \mathrm{tr}(\mathbf{T}\cdot\nabla\vec{v})\mathrm{d}V \tag{8}$$

with chemical potential now expressed on a molar basis and N_k representing the total number of moles of component k in the system. Unlike our previous analysis,[3] we have no need to assume incompressibility in this step.

For convenience, we can express[6] $\mathbf{T}$ in terms of an isotropic "bulk" pressure P^{b} and an osmotic stress $\mathbf{S}$:

10.1021/ma020225p CCC: $22.00

$$\mathbf{T} = -P^{b}\mathbf{I} + \mathbf{S} \tag{9}$$

Using this and another form of the transport theorem (ref 5, p 21), eq 8 becomes

$$\frac{dA}{dt} = -P^{b}\frac{dV}{dt} + \sum_{k}\mu_{k}^{b}\frac{dN_{k}}{dt} + \int_{V}\mathrm{tr}(\mathbf{S}\cdot\nabla\vec{v})\,dV \tag{10}$$

For systems consisting of only homogeneous (bulk) phases (i.e., no interphases), the osmotic stress must be zero so that we obtain

$$\delta A = -P^{b}\delta V + \sum_{k}\mu_{k}^{b}\delta N_{k} \quad \text{(no interphases)} \tag{11}$$

as expected. Thus, the domain for the integral in the last term in eq 10 reduces to just that of the interphase, V_I.

Compression of a Planar Interphase

We now consider a specific case of compression of a polymer interphase contained in the gap between two impenetrable planar surfaces.[4] Pure compression is irrotational, so in this case (ref 5 p 39) $\nabla\vec{v}$ is identical to the rate of deformation tensor **D** with components (ref 7, p 122)

$$D_{ii} = \frac{1}{\lambda_{i}}\frac{d\lambda_{i}}{dt} \tag{12}$$

where the dilations λ_i are the stretched lengths of line segments in the principal directions ($i = x, y, z$) having unit length in the initial undeformed state.

Assuming axisymmetric compression in the z-direction, the osmotic stress tensor must have the form

$$\begin{aligned}\mathbf{S} &= S_{xx}(\vec{e}_{x}\vec{e}_{x} + \vec{e}_{y}\vec{e}_{y}) + S_{zz}\vec{e}_{z}\vec{e}_{z}\\ &= S_{I}\mathbf{I} + S_{D}\left(-\frac{1}{2}\vec{e}_{x}\vec{e}_{x} - \frac{1}{2}\vec{e}_{y}\vec{e}_{y} + \vec{e}_{z}\vec{e}_{z}\right)\end{aligned} \tag{13}$$

The second form of eq 13 decomposes **S** into isotropic (mean) and deviatoric parts with components

$$S_{I} = \frac{2}{3}S_{xx} + \frac{1}{3}S_{zz} \equiv -(\Pi - \Pi^{b}), \quad S_{D} = \frac{2}{3}(S_{zz} - S_{xx}) \tag{14}$$

The isotropic part must be identified as the osmotic pressure difference ($\Pi - \Pi^b$), while the deviatoric part accounts for deformations at constant volume since it has zero trace.[4] Substitution of eqs 12−14 into eq 10, as well as generalization of the time derivatives into differential variations using the chain rule, yields

$$\delta A = -P^{b}\delta V + \sum_{k}\mu_{k}^{b}\delta N_{k} + \int_{V_{I}}\left\{(\Pi^{b} - \Pi)\frac{\delta\lambda_{V}}{\lambda_{V}} + S_{D}\left[\frac{\delta\lambda_{z}}{\lambda_{z}} - \frac{1}{2}\frac{\delta\lambda_{A}}{\lambda_{A}}\right]\right\}dV \tag{15}$$

where $\lambda_A \equiv \lambda_x\lambda_y$ and $\lambda_V \equiv \lambda_x\lambda_y\lambda_z = \lambda_A\lambda_z$.

The volume integration is problematic because the domain V_I changes with the deformation. The definition of volumetric dilation, $dV \equiv \lambda_V dV_R$, transforms the integration domain into an unchanging reference configuration. Thus

$$\int_{V_{I}}\left\{(\Pi^{b} - \Pi)\frac{\delta\lambda_{V}}{\lambda_{V}} + S_{D}\left[\frac{\delta\lambda_{z}}{\lambda_{z}} - \frac{1}{2}\frac{\delta\lambda_{A}}{\lambda_{A}}\right]\right\}dV = \int_{V_{I,R}}\left\{(\Pi^{b} - \Pi)\delta\lambda_{V} + S_{D}\left[\lambda_{A}\delta\lambda_{z} - \frac{1}{2}\lambda_{z}\delta\lambda_{A}\right]\right\}dV_{R} \tag{16}$$

The domain transformation also allows us to treat variations of functionals $f(\bullet)$ according to

$$\delta\int_{V_{I}}f(\bullet)\,dV = \int_{V_{I,R}}\delta[\lambda f(\bullet)]\,dV_{R} \tag{17}$$

After some further chain rule manipulations of the integrand of eq 16, transformation back to the original domain, and use of eq 17, eq 15 becomes

$$\delta A = -P^{b}\delta V + \sum_{k}\mu_{k}^{b}\delta N_{k} + \delta\int_{V_{I}}\left(\Pi^{b} - \Pi + \frac{S_{D}}{2}\right)dV + \int_{V_{I}}\left[-\delta(\Pi^{b} - \Pi) + \frac{\delta(S_{D}\lambda_{z})}{2\lambda_{z}} - \frac{\delta(S_{D}\lambda_{A})}{\lambda_{A}}\right]dV \tag{18}$$

as found previously by Evans.[4]

Interfacial Tension and Disjoining Pressure

The interphase under consideration occupies the region between parallel planar surfaces separated by a gap distance $2z_m$. Each surface has area A_s. For simplicity, we shall ignore edge effects and lateral ($x - y$) property variations, and assume symmetry of the interphase about the central plane at $z = z_m$. The interfacial tension is defined by

$$\gamma \equiv \frac{1}{2}\left(\frac{\delta A}{\delta A_{s}}\right)_{T,V,N_{k},z_{m}} \tag{19}$$

with the factor of one-half accounting for two surfaces. The disjoining pressure is

$$\pi \equiv -\frac{1}{2A_{s}}\left(\frac{\delta A}{\delta z_{m}}\right)_{T,V,N_{k},A_{s}} \tag{20}$$

We can evaluate these quantities using eq 18, recognizing the need for eq 17 to handle some terms. The complete derivations are available as Supporting Information. The interfacial tension and disjoining pressure simplify to

$$\gamma = \int_{0}^{z_{m}}\left(\Pi^{b} - \Pi - \frac{S_{D}}{2}\right)dV \tag{21}$$

and

$$\pi = \Pi^{m} - \Pi^{b} - S_{D}^{m} \tag{22}$$

where superscript m denotes evaluation at $z = z_m$.

Finally, we must choose a value for S_D. For interphase compression that proceeds so slowly that every state is as an equilibrium state (full equilibrium[3,4]), the interfacial tension has the correct Kirkwood−Buff form if we set $S_D \equiv 0$. In this case, the disjoining pressure equals the osmotic pressure difference between the gap midpoint and bulk solution, a result in accord with that for electrostatic interactions between charged surfaces.[8,9]

For interphase compression subject to constraints, one must choose S_D in a way that ensures theoretical consistency. For example, self-consistent mean field

(SCMF) analyses of polymer interphases have considered compression under the constraint of constant polymer adsorbed mass per area (constrained equilibrium[3,4]). Under these conditions, SCMF theory yields interfacial tension having the form[3,4]

$$\gamma = \int_0^{z_m} (\Pi^b - \Pi - g\rho_p)\, dV \tag{23}$$

where ρ_p is the polymer density (mass or molar) and g is a Lagrange multiplier (with appropriate units) associated with the adsorbed polymer mass constraint. In this case, one must choose $S_D \equiv 2g\rho_p$. The disjoining pressure becomes

$$\pi = \Pi^m - \Pi^b - 2g\rho_p^m \tag{24}$$

The implications of these expressions for calculating the work associated with compression of polymer interphases have been discussed at length in previous publications.[3,4]

In particular, we must recognize that the work potential for compression of polymer−solvent mixtures between solid surfaces is *not* $A_s\delta\gamma$, as discussed by Evans[4] and Lyklema.[10] The work required to compress two opposing adsorbed polymer layers (for example, in the surface forces apparatus[1] or between two polymer-coated colloidal particles) does not equal the change in interfacial tension from infinite to finite surface separation.[11,12] Instead, the compression work equals the integral of the disjoining pressure evaluated at the midpoint between the surfaces (eq 24), at least for interactions of identical symmetric surfaces. In this regard, polymer-mediated forces between surfaces have exactly the same foundation as electrostatic forces, as has been established for many years.[1,8−10] Establishing this common foundation is a prerequisite for developing rigorous density functional models for coupled polymeric/electrostatic colloidal forces without invoking a “DLVO[1]-like” additivity assumption.

Supporting Information Available: Derivations of eqs 21 and 22 from eqs 18−20. This material is available free of charge via the Internet at http://pubs.acs.org.

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MA020225P