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Published in:
Journal of Chemical Physics

DOI:
[10.1063/1.475651](https://doi.org/10.1063/1.475651)

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Document Version
Publisher's PDF, also known as Version of record

Publication date:
1998

[Link to publication in University of Groningen/UMCG research database](#)

Citation for published version (APA):

Maurits, N. M., Zvelindovsky, A. V. M., & Fraaije, J. G. E. M. (1998). Equation of state and stress tensor in inhomogeneous compressible copolymer melts: Dynamic mean-field density functional approach. *Journal of Chemical Physics*, 108(6), 2638 - 2650. <https://doi.org/10.1063/1.475651>

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Citation: *J. Chem. Phys.* **108**, 2638 (1998); doi: 10.1063/1.475651

View online: <https://doi.org/10.1063/1.475651>

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Equation of state and stress tensor in inhomogeneous compressible copolymer melts: Dynamic mean-field density functional approach

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(Received 25 August 1997; accepted 3 November 1997)

We have derived an expression for the global stress in *inhomogeneous* complex copolymer liquids. We apply the principle of virtual work to the free energy as defined in the dynamic mean-field density functional method. This method automatically provides the full stress tensor (deviatoric and isotropic parts) and hence an equation of state for inhomogeneous compressible copolymer melts. The excluded volume interactions and cohesive interactions between chains have been explicitly taken into account. Therefore the expressions for the stress and thermodynamic pressure have a wide range of validity. The connectivity of the chains is automatically accounted for and the free energy adapts very well to changes in the molecule properties. In the limiting case of homogeneous systems it simplifies to known results. In order to study rheological properties of copolymer melts and npT -ensemble simulations, the pressure and stress components have to be calculated at any given moment in time. We show how the pressure and stress can be numerically evaluated during simulations using a Green propagator algorithm, instead of having to calculate the time dependent configuration distribution function explicitly from a Smoluchowski equation. We provide illustrative numerical results that indicate how the pressure changes during microphase separation.

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I. INTRODUCTION

A. General

The dynamic mean-field density functional method is a method for numerically calculating the phase-separation dynamics of copolymer liquids in 3D. It predicts morphologies and has recently been successfully used to predict part of a Pluronic/water phase diagram.¹ The method is based upon a generalized time-dependent Ginzburg-Landau theory for conserved order parameter of the following general form:²⁻⁴

$$\begin{aligned} \frac{\partial \rho_I(\mathbf{r})}{\partial t} = & \sum_{J=1}^M \int_V \mathcal{D}_{IJ}(\mathbf{r}, \mathbf{r}_1) \mu_J(\mathbf{r}_1) d\mathbf{r}_1 \\ & - \beta^{-1} \sum_{J=1}^M \int_V \frac{\delta \mathcal{D}_{IJ}(\mathbf{r}, \mathbf{r}_1)}{\delta \rho_J(\mathbf{r}_1)} d\mathbf{r}_1 + \eta_I(\mathbf{r}, t), \end{aligned} \quad (1)$$

$$\mathcal{D}_{IJ}(\mathbf{r}, \mathbf{r}_1) = \nabla_{\mathbf{r}} \cdot \Lambda_{IJ}(\mathbf{r}, \mathbf{r}_1) \nabla_{\mathbf{r}_1},$$

with particle concentration fields $\rho_I(\mathbf{r})$ ($I=1, \dots, M$), Onsager kinetic coefficients Λ_{IJ} , intrinsic chemical potentials $\mu_I \equiv \delta F / \delta \rho_I(\mathbf{r})$ (F is the free energy), $\beta^{-1} = k_B T$ and noise fields $\eta_I(\mathbf{r}, t)$. The noise has a Gaussian distribution with moments dictated by a fluctuation-dissipation theorem.⁴⁻⁶

The goal of mesoscopic modelling is to obtain a theory of ordering phenomena in polymer liquids, based on a "molecular" description. We use a free energy functional for a collection of Gaussian chains in a mean-field environment.^{7,8} In this approach we try to retain as much as possible of the underlying molecular detail, e.g. the architecture and compo-

sition of the chain molecules. To this end, we do not use a phenomenological expansion of the free energy in the order parameters, as is commonly done in Ginzburg-Landau models,^{2,3,9-12} but define an intrinsic free energy functional based on a density distribution function that results from a minimization criterion.¹³ This introduces external potentials as Lagrange multiplier fields. The density (particle concentration) fields and external potential fields are coupled one-to-one through the density functional. In this approach the free energy immediately reflects changes in the molecular properties which enables practical application of the method. Some results of numerical calculations of phase separation in *incompressible* block copolymer melts and concentrated surfactant solutions were already discussed in Refs. 13 and 14. The method has been extended to include *compressible* melts¹⁵ and nonlocal kinetic coefficients.¹⁶

In this paper we have derived an expression for the global stress in *inhomogeneous* complex copolymer liquids which, in the limiting case of homogeneous systems, is analogous to the expression for the stress tensor that was derived by Doi and Edwards.⁷ This expression was obtained from a configurational average of microscopic stresses where the distribution function results from a Smoluchowski equation in the presence of homogeneous flow. To this end, we employ the principle of virtual work on the free energy as defined in the dynamic mean-field density functional method. This method provides an expression for the total stress tensor and hence from its trace an expression for the thermodynamic pressure i.e., an equation of state for inhomogeneous copolymer melts. Before we explain the details of the derivation, we first discuss previous studies on equa-

tions of state and stress tensors for (in)homogeneous copolymer melts.

B. Equations of state

Equations of state for chain molecules are usually limited to *homogeneous* systems and often contain severe simplifications regarding connectivity. In Ref. 17, the connectivity is taken into account by allowing only a limited number of degrees of freedom (less than 3) for chain elements (by use of the so-called Prigogine parameter c). In this cell model, the Prigogine parameter determines the expression for the free volume per chain. Several authors have tried to improve the cell model by including geometry factors in the free volume expression,¹⁸ by using different expressions for the mean potential energy per mer¹⁹ or by including the possibility of empty sites.²⁰ The lattice-fluid model developed in Ref. 21 that puts chains on a lattice in order to be able to calculate the partition function, is improved in Ref. 22 by including molecular shape differences and in Ref. 23 by including entropy contributions.

The lattice theories of Flory and Huggins^{24,25} are generalized to continuous space in Ref. 26. The complete disregard for chain structure is first improved in Ref. 27 by relating the compressibility factor of an n -mer fluid to compressibility factors of monomer and dimer fluids at the same volume fraction. In Ref. 28 the theory in Ref. 27 is further improved by including structural information for a diatomic fluid, using site-site correlation functions at contact, which results in a modified thermodynamic perturbation theory. These studies are all restricted to athermal *homogeneous* melts.

Monte-Carlo simulations of lattice models for polymer melts are employed in Refs. 29 and 30 to measure the chemical potential by a particle-insertion method. This enables calculation of the osmotic pressure by thermodynamic integration.

C. Stress tensor

Expressions for the stress in a viscoelastic material usually serve the purpose of analyzing theoretical and experimental results.^{8,31} Many authors study stress-strain relationships in order to access the rheological properties of the material. The methods that are used to derive expressions for the stress (given a Hamiltonian) date back to the sixties and seventies. A few different approaches can be discerned.

In Ref. 3 stochastic equations are given for low molecular weight fluids. These equations (or other hydrodynamic equations valid for fluids in a two-phase region³²) can be combined with the fluid momentum balance equation. This allows for a relationship to be derived between the Hamiltonian of the system and the divergence of the stress tensor. If the Hamiltonian is a spatial average of a local function, a compatible local stress tensor can be derived^{32–39} which is unique up to a divergence free field. The local stress tensor can be spatially averaged to obtain an expression for the average shear stress.^{34,40,41} Similar expressions are also used in inhomogeneous systems as a measure of the spatial anisotropy of domains distorted by shear flow.^{36,42,43} The average

shear stress may also be expressed in terms of the nonequilibrium structure factor.^{36,40,44} The total stress of the material is often composed of this “anisotropy” factor, a separate viscous contribution and a (hydrodynamic) pressure contribution.^{35,36,42,43,45,46}

Another approach to viscoelasticity is to consider the viscoelastic polymeric material as a collection of particles suspended in a viscous solvent. The stress is then composed of the usual viscous solvent part and a microscopic contribution due to the forces between interacting particles.^{7,47–49}

A more thermodynamic approach is taken in Ref. 50 for solutions of rodlike polymers, in Ref. 44 for homogeneous polymer melts, in Ref. 51 for liquid crystals and in Ref. 52 for critical liquids. Here the principle of virtual work is applied to find the stress tensor by calculating the elastic response of a material to a small deformation.

In this paper we generalize the expression for the stress tensor⁷ to the case of compressible inhomogeneous complex copolymer liquids. The dynamical free energy $\mathcal{A}$ as considered in Ref. 7 accounts for entropy effects of ideal beads and energy effects due to the potential field H :

$$\mathcal{A} \equiv \int d\mathbf{R} \psi(k_B T \ln \psi + H). \quad (2)$$

Here, ψ is the distribution function of the beads. According to the principle of virtual work, the stress $\sigma_{\alpha\beta}^{(p)}$ due to the particles is related to a change in the dynamical free energy. The formal application of the principle of virtual work is not hard since the dynamical free energy is simple (ideal polymers only) and an expression for the variation of the distribution function ψ can be obtained from a simplified Smoluchowski equation that is dominated by the velocity gradients due to the deformation. This leads to^{7,48}

$$\sigma_{\alpha\beta}^{(p)} = -\frac{1}{V} \sum_m \langle F_{m\alpha} R_{m\beta} \rangle, \quad (3)$$

which is also found by considering the microscopic forces between beads. $F_{m\alpha}$ is the α -component of the nonhydrodynamic forces acting on bead m , $R_{m\beta}$ is the β -component of the position of bead m and the configurational average $\langle \cdot \rangle$ is taken with respect to ψ . If the interaction potential between beads is harmonic (Gaussian chain model), the particle contribution to the stress is given by

$$\sigma_{\alpha\beta}^{(p)} = \frac{n3}{Va^2} \sum_{n=1}^{N-1} \langle (\mathbf{R}_{n+1} - \mathbf{R}_n)_\alpha (\mathbf{R}_{n+1} - \mathbf{R}_n)_\beta \rangle. \quad (4)$$

Since only incompressible fluids are considered, isotropic stress contributions are dropped. Excluded volume potentials only affect the stress expression through the distribution function ψ . A basic assumption in the derivation is that even in the highly entangled state the “short-time” polymer dynamics (which completely determine the stress tensor) is governed by the Rouse model.

D. Present paper

We apply the principle of virtual work to the free energy functional as defined in the dynamic mean-field density functional theory^{13,53} to obtain an expression for the stress tensor in compressible inhomogeneous copolymer melts. In the limit of homogeneous systems, we obtain an expression analogous to Eq. (4). Moreover, employing the principle of virtual work immediately leads to an expression for the diagonal components of the stress tensor as well and therefore to an expression for the pressure (equation of state).

We show that our mathematical procedures are consistent by deriving the pressure not only by using the principle of virtual work, but also by calculating the change in free energy that results from an infinitesimal volume change. To our knowledge there have been no attempts to define an equation of state that includes molecular detail for general inhomogeneous compressible copolymer melts. In our model the connectivity of the chains is automatically accounted for and the free energy adapts very well to changes in the molecule properties. The free energy functional contains both excluded volume and cohesive interactions. The inhomogeneity of the system introduces an external potential as a Lagrange multiplier field from an optimization criterion (for details see Ref. 13). This external potential does not explicitly contribute to the expression for the stress tensor but changes the distribution function as will be explained in Sec. II C.

Previous simulations of phase separation in block copolymer melts using dynamic density functional theory (see e.g., Ref. 13) were always performed in an nVT -ensemble, since the volume of the simulation box remained constant. Simulations in an npT -ensemble will increase the relevance of numerical experiments compared to laboratory experiments, which are usually performed under constant pressure conditions. We intend to use a pressure coupling algorithm during simulations to keep the pressure constant. We show that the pressure for a homogeneous melt may be calculated analytically and can hence be used as the reference pressure in a pressure coupling algorithm in the near future. We shortly discuss an algorithm for numerically evaluating the pressure during a simulation that uses Green propagators. As a proof of concept, we show some numerical results that indicate how the pressure changes during microphase separation. The Green propagator algorithm avoids the use of a Smoluchowski equation to determine the configuration distribution function and can just as well be used to calculate the stress. The expression for the stress will be used in a future publication to study stress-strain relationships in a sheared melt.⁵⁴

II. THEORY

A. Dynamic mean-field density functional theory

We shortly repeat the main part of the theory of the mesoscopic dynamics algorithms in order to be able to explain the detailed derivation of the stress tensor and the results of the numerical calculations. We consider a melt of volume V , containing n diblock copolymers modeled as Gaussian chains, each of length $N = N_A + N_B$. There are two

concentration fields $\rho_A(\mathbf{r})$ and $\rho_B(\mathbf{r})$. Given these concentration fields a free energy functional $F[\rho]$ can be defined as follows:¹³

$$F[\rho] = -\frac{1}{\beta} \ln \frac{\Phi^n}{n!} - \sum_I \int U_I(\mathbf{r}) \rho_I(\mathbf{r}) d\mathbf{r} + F^{\text{nid}}[\rho]. \quad (5)$$

Here $F^{\text{nid}}[\rho]$ is the contribution from the non-ideal interactions and Φ is the partition functional for the ideal Gaussian chains in the external field U_I ,

$$\Phi \equiv \mathcal{N} \int_{V^N} e^{-\beta \left[H^G + \sum_{s'=1}^N U_{s'}(\mathbf{R}_{s'}) \right]} d\mathbf{R}_1 \cdots d\mathbf{R}_N, \quad (6)$$

where $\mathcal{N}$ is a normalization constant equal to $(1/\Lambda^3) (3/(2\pi a^2))^{\frac{3}{2}(N-1)}$, $\mathbf{R}_i = (X_i, Y_i, Z_i)$ is the position of the i -th bead in the chain and H^G is the Gaussian chain Hamiltonian [cf. H in Eq. (2)]

$$H^G = \frac{3}{2\beta a^2} \sum_{s=2}^N (\mathbf{R}_s - \mathbf{R}_{s-1})^2, \quad (7)$$

with a the Gaussian bond length parameter. The dynamical free energy as used in Doi and Edwards⁷ [Eq. (2)] is basically equal to the first term in Eq. (5) except that the external field now influences the distribution function. The free energy functional is derived from an optimization criterion¹³ which introduces the external potential as a Lagrange multiplier field. Notice that the inhomogeneity of the melt is reflected in the value of the external potentials. The external potentials and the concentration fields are related via a bijective density functional for ideal Gaussian chains:¹³

$$\rho_I[U](\mathbf{r}) = \frac{n \mathcal{N}}{\Phi} \sum_{s''=1}^N \delta_{Is''}^K \int_{V^N} \delta(\mathbf{r} - \mathbf{R}_{s''}) \times e^{-\beta \left[H^G + \sum_{s'=1}^N U_{s'}(\mathbf{R}_{s'}) \right]} d\mathbf{R}_1 \cdots d\mathbf{R}_N. \quad (8)$$

Here $\delta_{Is''}^K$ is a Kronecker delta with value 1 if bead s'' is of type I and 0 otherwise, $\exp(-\beta[H^G + \sum_{s'=1}^N U_{s'}(\mathbf{R}_{s'})])/\Phi$ is the single chain configuration distribution function.

The non-ideal free energy functional is formally split into two parts¹³

$$F^{\text{nid}}[\rho] = F^c[\rho] + F^e[\rho], \quad (9)$$

where F^e contains the excluded volume interactions, and F^c the cohesive interactions. The intrinsic chemical potentials μ_I^e and μ_I^c are defined by the functional derivatives of the free energy:

$$\begin{aligned} \mu_I(\mathbf{r}) &\equiv \frac{\delta F}{\delta \rho_I(\mathbf{r})} = -U_I(\mathbf{r}) + \frac{\delta F^c}{\delta \rho_I(\mathbf{r})} + \frac{\delta F^e}{\delta \rho_I(\mathbf{r})} \\ &= -U_I(\mathbf{r}) + \mu_I^c(\mathbf{r}) + \mu_I^e(\mathbf{r}). \end{aligned} \quad (10)$$

For the cohesive interactions we employ a two-body mean-field potential:

$$F^c[\rho] = \frac{1}{2} \sum_{IJ} \int_V \int_V \epsilon_{IJ}(|\mathbf{r} - \mathbf{r}'|) \rho_I(\mathbf{r}) \rho_J(\mathbf{r}') d\mathbf{r} d\mathbf{r}', \quad (11)$$

where $\epsilon_{IJ}(|\mathbf{r} - \mathbf{r}'|) = \epsilon_{JI}(|\mathbf{r} - \mathbf{r}'|)$ is a cohesive interaction between beads of type I at $\mathbf{r}$ and J at $\mathbf{r}'$, defined by the same Gaussian kernel as in the ideal Gaussian chain Hamiltonian

$$\epsilon_{IJ}(|\mathbf{r} - \mathbf{r}'|) \equiv \epsilon_{IJ}^0 \left(\frac{3}{2\pi a^2} \right)^{3/2} e^{-(3/(2a^2))(\mathbf{r} - \mathbf{r}')^2}. \quad (12)$$

In Ref. 15 we have shown that a very simple cell model can be used for excluded volume effects. In this case

$$F^e[\rho] = -\frac{1}{\beta} \sum_J \int_V \rho_J(\mathbf{r}) \ln \left(1 - \left(\sum_K \nu_K \rho_K(\mathbf{r}) \right)^{1/3} \right)^3 d\mathbf{r}. \quad (13)$$

Here ν_K is the bead volume. Notice that the models for F^c and F^e are not unique.¹⁵ However, the principle of virtual work can be applied to any model for the free energy and the resulting expression for the stress tensor will be model dependent. For practical applications, a Helfand penalty potential^{15,55} can be used, which allows for small density fluctuations around the mean bulk density. In this case the non-ideal free energy functional is given by

$$F^{\text{nid}}[\rho] = \frac{1}{2} \sum_{IJ} \int_V \int_V \Delta \epsilon_{IJ}(|\mathbf{r} - \mathbf{r}'|) \rho_I(\mathbf{r}) \rho_J(\mathbf{r}') d\mathbf{r} d\mathbf{r}' + \frac{\kappa_H}{2} \int_V \left(\sum_I \nu_I \rho_I(\mathbf{r}) - \sum_I \nu_I \rho_I^0 \right)^2 d\mathbf{r}, \quad (14)$$

where κ_H is a compressibility parameter, ρ_I^0 is the density of component I in the homogeneous melt and $\Delta \epsilon_{IJ} = \frac{1}{2}(\epsilon_{IJ} + \epsilon_{JI} - \epsilon_{II} - \epsilon_{JJ})$ is an exchange interaction parameter.

In equilibrium $\mu_I(\mathbf{r})$ is constant; this yields the familiar self-consistent field equations for Gaussian chains, given a proper choice for F^{nid} . When the system is not in equilibrium the gradient of the intrinsic chemical potential $-\nabla \mu_I$ acts as a thermodynamic force which drives collective relaxation processes. When the Onsager coefficients are constant the stochastic diffusion equations are of the following form

$$\frac{\partial \rho_I}{\partial t} = -\nabla \cdot \mathbf{J}_I, \quad (15)$$

$$\mathbf{J}_I = -M \nabla \mu_I + \tilde{\mathbf{J}}_I, \quad (16)$$

where M is a mobility coefficient and $\tilde{\mathbf{J}}_I$ is a noise field, distributed according to a fluctuation-dissipation theorem.⁴ Equations (15) and (16) form a well-established model to describe relaxation kinetics in polymer melts^{56–58} and have been used before in the context of dynamic mean-field functional theory to numerically calculate the phase-separation dynamics of copolymer liquids in 3D.^{1,13} Nonlocal forms for the Onsager coefficients have been studied in Ref. 16.

B. Principle of virtual work

A complex liquid or viscoelastic material possesses both elastic and viscous properties. If we apply an external force to a polymeric material the response of the system is related to the internal stress which is, in principle, a complex interplay between viscous and elastic stresses. In principle the viscous and elastic stresses can not easily be separated and several constitutive equations have been proposed to relate the stress tensor to the history of the applied strains (or strain rates) via complex stress relaxation functions.^{59,60} Constitutive equation are needed to calculate the flow of a fluid when an external force is applied. If the system is in the regime of linear viscoelasticity, the stress is small and the constitutive equation is a linear relationship between stress and strain. However, the scope of this paper is not to show how to calculate the dynamic behavior of a copolymer melt in an external flow field. We will postpone this discussion to a future publication.

The stress tensor σ_{ij} , of which the ij -component describes the i -component of the force per unit area perpendicular to the x_j -axis, can be defined by considering the work done by internal stresses if a body is undergoing a *small* deformation (the *principle of virtual work*, see e.g., Ref. 7). Suppose the deformation displaces the point r_α on the material to $r_\alpha + \delta \epsilon_{\alpha\beta} r_\beta$. Here, $\epsilon_{\alpha\beta} = \partial \mathbf{u}_\alpha / \partial r_\beta$ is the $\alpha\beta$ -component of the (unsymmetrized) strain tensor and $\mathbf{u}$ is the displacement vector.⁶¹ Then it can be shown that the related change in free energy F is given by:

$$\delta F = \sigma_{\alpha\beta} \delta \epsilon_{\alpha\beta} V. \quad (17)$$

Hence, by applying a small deformation to a body and calculating the change in free energy in the limit of this deformation going to zero, we can calculate the stress tensor σ_{ij} given the free energy F . Notice that the deformation must be applied slow enough to ensure that before *and* after the deformation the system is in thermodynamic equilibrium, i.e., the distribution function ψ changes but remains optimal.

The stress tensor as defined in Eq. (17) can be rewritten in terms of the symmetrized strain tensor $u_{\alpha\beta} \equiv \frac{1}{2}(\epsilon_{\alpha\beta} + \epsilon_{\beta\alpha})$.⁶¹

$$\sigma_{ij} \equiv \frac{1}{V} \left(\frac{\delta F}{\delta u_{ij}} \right)_T. \quad (18)$$

Notice that we have explicitly indicated the volume here.

C. The stress tensor and pressure in inhomogeneous compressible copolymer melts

1. Calculation of the stress tensor from first principles

The ij -component of the stress tensor σ_{ij} can be derived by employing the principle of virtual work [Eq. (17)]. We consider a cubic volume V with a density pattern $\{\rho_I\}$. If we consider the special deformation of the cubic volume as sketched in Fig. 1(a), ϵ_{xy} is the only element of the (unsymmetrized) strain tensor which is not zero. Since α is small we have $\epsilon_{xy} = \tan \alpha = \alpha$. This deformation allows us to calculate σ_{xy} . Since the system is in thermodynamic equilibrium be-

FIG. 1. (a) Virtual deformation applied to a cubic volume V in order to calculate σ_{xy} . The volume V is preserved. (b) Virtual deformation applied to a cubic volume V in order to calculate σ_{xx} . The volume V is not preserved.

fore and after the deformation (but not necessarily in a free energy minimum), the distribution function ψ changes to remain optimal. Hence the densities and the external potentials are different before and after the deformation.

In Appendix A we show that the principle of virtual work applied to the non-ideal free energy (9) due to the cohesive interactions (using the cell model) leads to

$$\begin{aligned} \delta F^{\text{nid}} &= F^{\text{nid}}[\tilde{\rho}] - F^{\text{nid}}[\rho] \\ &= -\frac{3}{2a^2} \sum_{IJ} \int_V \int_V \epsilon_{IJ}(|\mathbf{r}_1 - \mathbf{r}_2|) \alpha (x_1 - x_2) \\ &\quad \times (y_1 - y_2) \rho_I(\mathbf{r}_1) \rho_J(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2. \end{aligned} \quad (19)$$

The excluded volume interactions, which are local, only influence the *isotropic* stress (see also Ref. 7) because the deviatoric stress is completely determined by intra- and intermolecular *nonlocal* forces.

The principle of virtual work applied to the ideal free energy leads to (see Appendix A)

$$\begin{aligned} \delta F^{\text{id}} &= \frac{n\mathcal{N}}{\beta\Phi} \int_{V^N} e^{-(3/(2a^2)) \sum_{s=2}^N (\mathbf{R}_s - \mathbf{R}_{s-1})^2 - \beta \sum_{s'=1}^N U_{s'}(\mathbf{R}_{s'})} \\ &\quad \times \frac{3\alpha}{a^2} \sum_{s=2}^N (X_s - X_{s-1})(Y_s - Y_{s-1}) \\ &\quad \times d\mathbf{R}_1 \cdots d\mathbf{R}_N \\ &= \frac{3n\alpha}{a^2\beta} \left\langle \sum_{s=2}^N (X_s - X_{s-1})(Y_s - Y_{s-1}) \right\rangle. \end{aligned} \quad (20)$$

Here, the ensemble average $\langle \rangle$ is taken with respect to the Boltzmann weight $\exp[-(3/(2a^2)) \sum_{s=2}^N (\mathbf{R}_s - \mathbf{R}_{s-1})^2 - \beta \sum_{s'=1}^N U_{s'}(\mathbf{R}_{s'})]$ which includes the external potential so that the inhomogeneity of the system is automatically taken into account. Since, by definition, we have for the special deformation under consideration

$$\delta F = \sigma_{xy} \delta \epsilon_{xy} V = \sigma_{xy} \alpha V, \quad (21)$$

we find the final result

$$\begin{aligned} \sigma_{xy} &= \frac{3n}{a^2\beta V} \left\langle \sum_{s=2}^N (X_s - X_{s-1})(Y_s - Y_{s-1}) \right\rangle \\ &\quad - \frac{3}{2a^2 V} \sum_{IJ} \int_V \int_V \epsilon_{IJ}(|\mathbf{r}_1 - \mathbf{r}_2|) (x_1 - x_2) \\ &\quad \times (y_1 - y_2) \rho_I(\mathbf{r}_1) \rho_J(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2. \end{aligned} \quad (22)$$

Notice that σ_{xy} explicitly depends on the entire density profile $\{\rho_I\}$ but only implicitly on the external potential $\{U_I\}$ via the Boltzmann weight. The other non-diagonal components of the stress tensor are very similar; for σ_{xz} the term $(X_s - X_{s-1})(Y_s - Y_{s-1})$ must be replaced by $(X_s - X_{s-1})(Z_s - Z_{s-1})$ and for σ_{yz} by $(Y_s - Y_{s-1})(Z_s - Z_{s-1})$ etc. The second part of σ_{xy} results from the nonlocal mean-field interactions, the first part of σ_{xy} results from the connectivity of the chains (orientation of the bond vectors) and is analogous to the result obtained for homogeneous concentrated polymer solutions.⁷ Notice however that the configurational average in Eq. (22) is taken with respect to the Boltzmann factor ψ that includes the external potential which accounts for the inhomogeneity in the system. The distribution function ψ in Eq. (2) is obtained from a Smoluchowski equation⁷ for a macroscopic velocity field using a Rouse dynamics model. In Sec. III A we show how Eq. (22) can be calculated in our framework of a generalized time-dependent Ginzburg-Landau model without explicitly considering a Smoluchowski equation for ψ . If the Helfand penalty potential instead of the cell model is considered, the interaction parameters ϵ_{IJ} have to be replaced by *exchange* interaction parameters $\Delta\epsilon_{IJ}$.

To determine the diagonal components of the stress tensor we consider deformations as indicated in Fig. 1(b). This particular deformation yields σ_{xx} since $\epsilon_{xx} = \alpha$ and all other components of the unsymmetrized strain tensor are zero. The details of the derivation of the diagonal components of the stress tensor are outlined in Appendix B.

In case of the cell model we get both an excluded volume and a cohesive interaction contribution from the non-ideal free energy to σ_{xx} . The ideal free energy now gives a contribution from the connectivity of the chains *and* an ideal gas contribution. We find for the diagonal component of the stress tensor (see Appendix B)

$$\begin{aligned} \sigma_{xx} &= -\frac{nN}{\beta V} + \frac{3n}{a^2\beta V} \left\langle \sum_{s=2}^N (X_s - X_{s-1})^2 \right\rangle \\ &\quad - \frac{3}{2a^2 V} \sum_{IJ} \int_V \int_V \epsilon_{IJ}(|\mathbf{r}_1 - \mathbf{r}_2|) (x_1 - x_2)^2 \\ &\quad \times \rho_I(\mathbf{r}_1) \rho_J(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 \\ &\quad - \frac{1}{\beta V} \sum_I \int_V \rho_I(\mathbf{r}) \frac{(\sum_I v_I \rho_I(\mathbf{r}))^{1/3}}{1 - (\sum_I v_I \rho_I(\mathbf{r}))^{1/3}} d\mathbf{r}. \end{aligned} \quad (23)$$

The stress tensor components σ_{yy} and σ_{zz} are very similar in that $(X_s - X_{s-1})^2$ must be replaced everywhere by $(Y_s - Y_{s-1})^2$ and $(Z_s - Z_{s-1})^2$ respectively, etc. In case the Helfand penalty model is considered the contribution from the non-ideal free energy to the diagonal component of the stress tensor is given by

$$\begin{aligned} \sigma_{xx}^{\text{nid}} = & -\frac{3}{2a^2V} \sum_{IJ} \int_V \int_V \Delta \epsilon_{IJ}(|\mathbf{r}_1 - \mathbf{r}_2|)(x_1 - x_2)^2 \\ & \times \rho_I(\mathbf{r}_1) \rho_J(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 \\ & - \frac{\kappa_H}{2V} \int_V \left(\sum_I v_I \rho_I(\mathbf{r}) - \sum_I v_I \rho_I^0 \right)^2 d\mathbf{r}. \end{aligned} \quad (24)$$

In Ref. 62 we have shown that most phenomenological free energy models (e.g., Oono-Puri or Cahn-Hilliard) can be obtained from the free energy (5) by a functional Taylor expansion that is truncated at different places. The free energy that is used in e.g., Refs. 33 and 37 to derive an expression for the stress is also contained in Eq. (5). Since the principle of virtual work can be applied to any free energy (functional)⁵² the expression for the stress tensor as found in Refs. 33 and 37 is automatically contained in our expressions (22) and (23). In principle, a direct (Taylor) expansion of Eqs. (22) or (23) combined with a fitting procedure should also yield phenomenological expressions for the stress. This procedure is rather cumbersome however and will not be dealt with in the present article.

2. Comparison trace of stress tensor and pressure

The operational definition of pressure is given by^{61,63}

$$\text{Tr} \sigma_{ij} = -3p. \quad (25)$$

For compressible materials p is also the thermodynamic pressure. This does not hold for incompressible materials where the pressure is merely a Lagrange multiplier (see also the discussion in Ref. 15). In an incompressible fluid, the isotropic part of the stress tensor is determined by external conditions only and therefore irrelevant in the discussion on viscoelastic properties of material. The thermodynamic pressure (in nVT -ensembles) is defined as follows

$$p^t \equiv - \left(\frac{\partial F}{\partial V} \right)_{N,T}. \quad (26)$$

We can check the consistency of our mathematical procedures for calculating the stress tensor by comparing the result for the pressure resulting from the thermodynamic definition (26) to the result for the pressure as obtained from Eq. (25). In Appendix C we show (for the cell model) that indeed $-\frac{1}{3}(\sigma_{xx} + \sigma_{yy} + \sigma_{zz}) = p^t$ as expected.

3. Homogeneous limiting case

Expression (C4) allows us to analytically calculate the pressure of a homogeneous copolymer melt ($U_I=0$, $\rho_I(\mathbf{r}) = nN_I/V$). For the cohesive interactions we employ¹³ $\epsilon_{IJ}(|\mathbf{r} - \mathbf{r}'|) = \epsilon_{IJ}^0 (3/(2\pi a^2))^{3/2} \exp[-(3/(2a^2))(\mathbf{r} - \mathbf{r}')^2]$ and hence:

$$\begin{aligned} p_h = & \frac{n}{\beta V} + \frac{1}{2} \sum_{IJ} \epsilon_{IJ}^0 \frac{n^2 N_I N_J}{V^2} \\ & + \frac{1}{\beta} \frac{\sum_I n N_I / V (\sum_J v_J n N_J / V)^{1/3}}{1 - (\sum_I v_I n N_I / V)^{1/3}}. \end{aligned} \quad (27)$$

Here, N_I is the number of beads of type I in one copolymer. In a homogeneous copolymer melt the non-diagonal components of the stress (22) are all zero because the distribution function is always assumed to be optimal. In an npT -simulation, expression (27) provides us with a reference pressure which may be used in a pressure coupling algorithm. A similar expression is easily obtained for the Helfand penalty potential (see also Sec. III B).

III. NUMERICAL MODEL

A. Calculation stress tensor and pressure

In our group we are presently studying the influence of shear on micro-phase pattern formation in copolymer melts.⁵⁴ In order to study the relationship (e.g., the elasticity moduli) between shear strain and stress (which is linear for purely elastic materials) we need to calculate the stress components numerically.

Also, because we aim at performing npT -ensemble simulations to study micro-phase separation processes under constant pressure conditions, we need to be able to calculate the pressure at any given moment in time numerically.

In order to be able to calculate the pressure and stress numerically, we define a Green propagator algorithm for calculating the ensemble average of the ideal Gaussian chain Hamiltonian and the ensemble average of the combined orientation of the bond vectors. This algorithm is slightly modified with respect to the algorithm that is used in calculating the density from the external potential. Notice that we do not employ a Smoluchowski equation for the time evolution of the single chain distribution function. Instead we obtain the external potential U_I implicitly from the dynamics equation for the density (15).

Define:

$$G^{\text{inv}}(\mathbf{r}, N+1) \equiv G(\mathbf{r}, 0) \equiv 1, \quad (28)$$

$$\begin{aligned} G^{\text{inv}}(\mathbf{r}, s) \equiv & e^{-\beta U_s(\mathbf{r})} \int_V \frac{e^{-(3/(2a^2))(\mathbf{r} - \mathbf{r}')^2}}{(2\pi a^2/3)^{3/2}} \\ & \times G^{\text{inv}}(\mathbf{r}', s+1) d\mathbf{r}', \end{aligned} \quad (29)$$

$$G(\mathbf{r}, s) \equiv e^{-\beta U_s(\mathbf{r})} \int_V \frac{e^{-(3/(2a^2))(\mathbf{r} - \mathbf{r}')^2}}{(2\pi a^2/3)^{3/2}} G(\mathbf{r}', s-1) d\mathbf{r}'. \quad (30)$$

Then

$$\begin{aligned} \frac{2n}{3V} \langle H^G \rangle &\equiv \frac{n}{V\beta\Lambda^3\Phi} \sum_{s=2}^N \int_V \int_V G^{\text{inv}}(\mathbf{r}, s) \\ &\times \frac{e^{-(3/(2a^2))(\mathbf{r}-\mathbf{r}')^2} (\mathbf{r}-\mathbf{r}')^2}{a^2(2\pi a^2/3)^{3/2}} \\ &\times G(\mathbf{r}', s-1) d\mathbf{r} d\mathbf{r}'. \end{aligned} \quad (31)$$

Similarly

$$\begin{aligned} \frac{3n}{a^2\beta V} \left\langle \sum_{s=2}^N (x_s - x_{s-1})(y_s - y_{s-1}) \right\rangle \\ \equiv \frac{3n}{V\beta\Lambda^3\Phi} \sum_{s=2}^N \int_V \int_V G^{\text{inv}}(\mathbf{r}, s) \\ \times \frac{e^{-(3/(2a^2))(\mathbf{r}-\mathbf{r}')^2} (x-x')(y-y')}{a^2(2\pi a^2/3)^{3/2}} G(\mathbf{r}', s-1) d\mathbf{r} d\mathbf{r}', \end{aligned} \quad (32)$$

Φ can easily be calculated by integrating the total density once more over the volume. Any integration over the volume is performed numerically by adding the values over all grid-points and multiplying by the grid cell volume. The calculation of Eq. (31) only requires the evaluation of $\mathcal{O}(N)$ integrals; the integrals $G^{\text{inv}}(\mathbf{r}, s)$ and $G(\mathbf{r}, s)$ can be calculated beforehand and stored in memory. The other parts in the definitions of the pressure and the stress are evaluated with-

out much computational effort and are either simple integrals or can be evaluated using the discrete stencil operator that is derived in Appendix D. In Ref. 64 we derived a stencil operator for numerically evaluating Eq. (29) and (30). Similarly, we have derived a stencil operator for numerically evaluating

$$\begin{aligned} \xi[f](\mathbf{r}) &\equiv \frac{1}{a^2} \left(\frac{3}{2\pi a^2} \right)^{3/2} \int_V e^{-(3/(2a^2))(\mathbf{r}-\mathbf{r}')^2} \\ &\times (\mathbf{r}-\mathbf{r}')^2 f(\mathbf{r}') d\mathbf{r}', \end{aligned} \quad (33)$$

in Appendix D. Since

$$\begin{aligned} \xi_{ij}[f](\mathbf{r}) &\equiv \frac{1}{a^2} \left(\frac{3}{2\pi a^2} \right)^{3/2} \int_V e^{-(3/(2a^2))(\mathbf{r}-\mathbf{r}')^2} (\mathbf{r}_i - \mathbf{r}'_i) \\ &\times (\mathbf{r}_j - \mathbf{r}'_j) f(\mathbf{r}') d\mathbf{r}', \end{aligned} \quad (34)$$

with Fourier transform

$$-\frac{a^2}{9} |\mathbf{q}_i| |\mathbf{q}_j| e^{-a^2 \mathbf{q}^2/6} f_{\mathbf{q}}, \quad (35)$$

does not possess spherical symmetry anymore it is hard to find an appropriate stencil operator to calculate the integral. The obvious discrete stencil to represent the particular symmetry of Eq. (35) would be ($i=x, j=y$)

$$\begin{aligned} (\xi_{xy, \mathbf{q}})_{\text{disc}} &\equiv c_0 + c_1 [\cos(q_x h) + \cos(q_y h) + \cos(q_z h)] + c_2 [\cos(q_x h - q_y h) + \cos(q_x h + q_y h)] + c_3 [\cos(q_x h - q_z h) \\ &+ \cos(q_x h + q_z h) + \cos(q_y h - q_z h) + \cos(q_y h + q_z h)] + c_4 [\cos(q_x h - q_y h - q_z h) + \cos(q_x h + q_y h - q_z h) \\ &+ \cos(q_x h - q_y h + q_z h) + \cos(q_x h + q_y h + q_z h)]. \end{aligned} \quad (36)$$

However, there are only 6 degrees of freedom in this stencil (including a/h) which is not sufficient to represent the rather complex behavior of Eq. (35) accurately. Since Eq. (34) only has to be calculated for analysis purposes we suggest to evaluate the integral in Fourier space.

B. Numerical results

As a proof of concept, we have performed a simulation of an aqueous Pluronic L64 ((EO)₁₃(PO)₃₀(EO)₁₃)¹ solution (60% polymer surfactant), during which we have calculated the pressure at every time step. We have used the Helfand penalty potential. For the Pluronic solution the dimensionless pressure is given by

$$\begin{aligned} \nu\beta p &\equiv \sum_I \theta_I^0 - \frac{f_P \sum_I \theta_I^0}{N\Lambda^3\Phi} \sum_{s=2}^N \int_V \int_V G^{\text{inv}}(\mathbf{r}, s) \\ &\times \frac{e^{-(3/(2a^2))(\mathbf{r}-\mathbf{r}')^2} (\mathbf{r}-\mathbf{r}')^2}{a^2(2\pi a^2/3)^{3/2}} G(\mathbf{r}', s-1) d\mathbf{r} d\mathbf{r}' \end{aligned}$$

$$\begin{aligned} &+ \frac{1}{2Va^2} \int_V \int_V \sum_{IJ} \chi_{IJ} \left(\frac{3}{2\pi a^2} \right)^{3/2} \\ &\times e^{-(3/a^2)(\mathbf{r}-\mathbf{r}')^2} (\mathbf{r}-\mathbf{r}')^2 \theta_I(\mathbf{r}) \theta_J(\mathbf{r}') d\mathbf{r} d\mathbf{r}' \\ &+ \frac{\kappa'_H}{2V} \int_V \left[\sum_I (\theta(\mathbf{r}) - \theta_I^0) \right]^2 d\mathbf{r}. \end{aligned} \quad (37)$$

The solvent ideal bead contribution has explicitly been included: f_P is the fraction of polymer surfactant in the solution and Φ_P is the Pluronic partition functional. κ'_H is the dimensionless compressibility parameter and the χ_{IJ} are dimensionless exchange interaction parameters. The Pluronic molecule is modeled as an $A_3B_9A_3$ ($N=15$) Gaussian chain (see Ref. 1) and the solvent molecules are modeled as single beads S .

Numerically, after discretizing the dynamic equations on a grid, we have the following Crank-Nicolson equations for each component I :

$$\theta_{Ir}^{k+1} - \omega \Delta \tau z_{Ir}^{k+1} = \theta_{Ir}^k + (1 - \omega) \Delta \tau z_{Ir}^k + \eta_{Ir}^k. \quad (38)$$

Here, η_{Ir}^k is the noise which is distributed according to a fluctuation-dissipation theorem.⁴ Notice that the noise is applied at every time step. z_r^k denotes the discretized diffusion part at time level k and (cubic) grid position r :

$$z_r = \sum_{\alpha} \sum_q d_{\alpha} [D_{\alpha} \theta_I D_{\alpha}]_{rq} \beta \mu_{Iq}. \quad (39)$$

D_{α} is the discretized diffusion operator in grid direction α and μ_{Iq} is evaluated at grid position q . ω is the Crank–Nicolson parameter and $\Delta \tau$ is a scaled time step. The Crank–Nicolson equations are solved iteratively at every time step using a steepest descent method for 1000 scaled time steps on a $64 \times 64 \times 64$ cubic grid. The initial system is homogeneous and is quenched at $\tau=0$. The compressibility parameter $\kappa_H' = 10$, the grid scaling $d = a/h = 1.15430$ and the total density $\sum_I \theta_I^0 = 1$. In the present simulation $\chi_{AB} = 3$, $\chi_{AS} = 1.4$ and $\chi_{BS} = 1.7$. All other parameters are taken as in Ref. 1.

Isosurface representations of $\theta_{PO} = 0.5$ at $\tau = 100$, $\tau = 200$ and $\tau = 1000$ are given in Fig. 2. In Fig. 3 we have plotted the time evolution of the volume-averaged order parameter w defined by:

$$w \equiv \frac{1}{V} \int_V (\theta_A^2 + \theta_B^2 + \theta_S^2) d\mathbf{r}. \quad (40)$$

As can be concluded from Figs. 2 and 3, the microphase separation process in the PL64 solution is proceeding very fast. After $\tau = 200$ the order parameter levels off, which shows that the main structures that develop in the phase separation process have already been formed at this time. Since the isosurfaces are at the same density-level, the very fast phase-separation process is also reflected in the fast growth of the structures until $\tau = 200$ in Fig. 2.

The pressure in the homogeneous melt can easily be calculated analytically:

$$\begin{aligned} \nu \beta p^{\text{hom}} &\equiv \sum_I \theta_I^0 - \frac{n_P(N-1)\nu}{V} + \frac{1}{2} \sum_{IJ} \chi_{IJ} \theta_I^0 \theta_J^0 \\ &= 1.0784. \end{aligned} \quad (41)$$

Notice that $n_P N \nu / V = f_P$. In Fig. 3 we have also plotted the time development of the global pressure in the melt. It is clearly visible that the pressure decreases as the order parameter increases; the pressure stabilizes once the main structures in the melt have been formed. The pressure decrease during phase-separation is caused by three simultaneous effects: (i) during phase separation the number of unfavorable AB, AS or BS contacts decreases which lowers the contribution from the cohesive interactions to the pressure, (ii) in interface areas the copolymer chains are stretched which increases $\langle H^G \rangle$ and hence lowers the pressure and (iii) the excluded volume interactions cause the system to decrease the local packing fraction at interfaces¹⁵ which leads to a decrease in the local pressure near interfaces and an increase in the local pressure in bulk phases.

FIG. 2. Isosurface representation of $\theta_{PO} = 0.5$ in a microphase separating aqueous Pluronic L64 ((EO)₁₃(PO)₃₀(EO)₁₃) solution (60% polymer surfactant). (a) $\tau = 100$; (b) $\tau = 200$; (c) $\tau = 1000$.

FIG. 3. Time-dependent micro-phase separation of an aqueous Pluronic L64 ((EO)₁₃(PO)₃₀(EO)₁₃) solution (60% polymer surfactant). The volume averaged order parameter ω (---) and dimensionless pressure $\nu\beta p$ (—) have been plotted as a function of the dimensionless time τ .

Since the pressure decreases in the present constant volume simulation, the corresponding constant pressure simulation would show a (small) decrease in volume. In many cases, micro-phase separation corresponds to a quench in temperature, and hence a decreasing volume should indeed be expected at constant pressure. The total decrease of the dimensionless pressure is about 6% (this number will depend on the choice for κ'_H). This corresponds to a small change in the volume at constant pressure. A rough estimate of the volume change at constant pressure can be obtained from the definition of the isothermal compressibility κ :

$$\kappa \equiv -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_T. \quad (42)$$

Since the change in the dimensionless pressure is approximately 0.067 and the dimensionless compressibility is equal to $\kappa = 1/\kappa'_H = 0.1$ we have that

$$\frac{\Delta V}{V} \approx -\kappa \Delta p = -0.0067. \quad (43)$$

Hence the volume decrease at constant pressure is less than one percent. It will be interesting to study the volume changes in phase separation in more detail; to this end we require more experimental data.

We will not further report on pressure coupling results in the present paper. However, since the pressure changes only slightly during micro-phase separation a stable pressure coupling algorithm (as used e.g., in molecular dynamics⁶⁵) should be feasible.

IV. CONCLUSION AND OUTLOOK

In this paper we have shown that an expression for the global stress in *inhomogeneous* complex copolymer liquids can be obtained which is analogous to the known expression for the stress in *homogeneous* complex fluids. We employ the principle of virtual work on the free energy as defined in the dynamic mean-field density functional method. This method was derived earlier in our group from generalized

time-dependent Ginzburg-Landau theory. The free energy is derived for a collection of Gaussian chains in a mean-field environment and includes both cohesive and excluded volume interactions. The connectivity of the chains is automatically accounted for and changes in the molecular properties are immediately reflected in the free energy and hence in the stress. The principle of virtual work leads to an expression for the full stress tensor. Since the trace of the stress tensor is related to the thermodynamic pressure, we immediately obtain an equation of state for inhomogeneous copolymer melts with the same flexible properties. The parametrizations of both the Gaussian chain molecular model and the mean-field interactions are crucial in this theory; a manuscript about improved parameters is currently in preparation.

We have developed a Green propagator algorithm to evaluate the expression for the thermodynamic pressure and used it to provide a global measure of pressure changes during a numerical simulation of a microphase separation process. The expression for the stress tensor will be used in a future publication to study the stress-strain relationship in a phase-separating copolymer melt under shear.⁵⁴ The analytical expression for the pressure in a homogeneous copolymer melt provides us with a reference pressure that can be used in a pressure-coupling method. This allows us to perform $n p T$ -ensemble simulations of micro-phase separation in the near future.

The expression for the pressure that was derived in this paper is global. For our purposes an expression for the global pressure (and stress) is sufficient. In literature there is ample discussion (see e.g., refs. 66–69) about the extent to which we can define uniquely local thermodynamic functions in an inhomogeneous system (at equilibrium). This can be done if the length scale of the inhomogeneity is macroscopic, but can not be done unambiguously if the characteristic length scale is on the scale of intermolecular forces, as in our systems. This is of interest, because we soon intend to include hydrodynamic effects into our simulations. The hydrodynamic effects will be discussed in detail in a future publication.

APPENDIX A: VIRTUAL WORK PRINCIPLE: DERIVATION OF THE NON-DIAGONAL COMPONENTS OF THE STRESS TENSOR

We have

$$\tilde{\rho}_I(x', y', z') = \tilde{\rho}_I(x + y \tan \alpha, y, z) = \rho_I(x, y, z), \quad (A1)$$

$$\begin{aligned} \tilde{U}_I(x', y', z') &= \tilde{U}_I(x + y \tan \alpha, y, z) \\ &\equiv U_I(x, y, z) + \Delta U_I(x, y, z), \end{aligned} \quad (A2)$$

where $\sim$ denotes fields and $\prime$ coordinates in the deformed volume $\tilde{V}$ [Fig. 1(a)]. As is shown below, there is no need to further specify the deviation $\Delta U_I(x, y, z)$ since it drops out of the calculations. We also have for small α

$$(\mathbf{r}'_1 - \mathbf{r}'_2)^2 = (\mathbf{r}_1 - \mathbf{r}_2)^2 + 2\alpha(x_1 - x_2)(y_1 - y_2). \quad (A3)$$

Using this we find for the principle of virtual work applied to the non-ideal free energy (9) due to the cohesive interactions

$$\begin{aligned}
F^{\text{nid}}[\tilde{\rho}] &= \frac{1}{2} \sum_{IJ} \int_{V'} \int_{V'} \epsilon_{IJ}(|\mathbf{r}'_1 - \mathbf{r}'_2|) \\
&\quad \times \tilde{\rho}_I(\mathbf{r}'_1) \tilde{\rho}_J(\mathbf{r}'_2) d\mathbf{r}'_1 d\mathbf{r}'_2 \\
&= \frac{1}{2} \sum_{IJ} \epsilon_{IJ}^0 \left(\frac{3}{2\pi a^2} \right)^{3/2} \int_V \int_V e^{-(3/(2a^2))(\mathbf{r}_1 - \mathbf{r}_2)^2} \\
&\quad \times \left(1 - \frac{3}{a^2} \alpha(x_1 - x_2)(y_1 - y_2) \right) \\
&\quad \times \rho_I(\mathbf{r}_1) \rho_J(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2, \tag{A4}
\end{aligned}$$

for small α and

$$\begin{aligned}
\delta F^{\text{nid}} &= F^{\text{nid}}[\tilde{\rho}] - F^{\text{nid}}[\rho] \\
&= -\frac{3}{2a^2} \sum_{IJ} \int_V \int_V \epsilon_{IJ}(|\mathbf{r}_1 - \mathbf{r}_2|) \alpha(x_1 - x_2) \\
&\quad \times (y_1 - y_2) \rho_I(\mathbf{r}_1) \rho_J(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2. \tag{A5}
\end{aligned}$$

A similar procedure gives $\delta F^e = 0$.

Now we consider the contribution to σ_{xy} from the ideal free energy in detail. First of all, we have for small α

$$\begin{aligned}
\Phi' &= \mathcal{N} \int_{V^N} e^{-(3/(2a^2)) \sum_{s=2}^N (\mathbf{R}'_s - \mathbf{R}'_{s-1})^2 - \beta \sum_{s'=1}^N \tilde{U}_{s'}(\mathbf{R}'_{s'})} \\
&\quad \times d\mathbf{R}'_1 \cdots d\mathbf{R}'_N \\
&= \mathcal{N} \int_{V^N} e^{-(3/(2a^2)) \sum_{s=2}^N (\mathbf{R}_s - \mathbf{R}_{s-1})^2} \left(1 - \frac{3}{2a^2} \sum_{s=2}^N \alpha \right. \\
&\quad \times (X_s - X_{s-1})(Y_s - Y_{s-1}) \left. \right) e^{-\beta \sum_{s'=1}^N U_{s'}(\mathbf{R}'_{s'})} \\
&\quad \times \left(1 - \beta \sum_{s'=1}^N \Delta U_{s'}(\mathbf{R}_{s'}) \right) d\mathbf{R}_1 \cdots d\mathbf{R}_N \\
&= \Phi \left(1 - \frac{\mathcal{N}}{\Phi} \int_{V^N} e^{-(3/(2a^2)) \sum_{s=2}^N (\mathbf{R}_s - \mathbf{R}_{s-1})^2 - \beta \sum_{s'=1}^N U_{s'}(\mathbf{R}_{s'})} \right. \\
&\quad \times \left. \left(\frac{3\alpha}{a^2} \sum_{s=2}^N (X_s - X_{s-1})(Y_s - Y_{s-1}) \right. \right. \\
&\quad \left. \left. + \beta \sum_{s'=1}^N \Delta U_{s'}(\mathbf{R}_{s'}) \right) d\mathbf{R}_1 \cdots d\mathbf{R}_N \right). \tag{A6}
\end{aligned}$$

Therefore the deviation of the first part of the ideal free energy in Eq. (5) leads to

$$\begin{aligned}
&\delta \left(-\frac{n}{\beta} \ln \Phi \right) \\
&= -\frac{n}{\beta} \frac{\Phi'}{\Phi} \\
&= \frac{n\mathcal{N}}{\beta\Phi} \int_{V^N} e^{-(3/(2a^2)) \sum_{s=2}^N (\mathbf{R}_s - \mathbf{R}_{s-1})^2 - \beta \sum_{s'=1}^N U_{s'}(\mathbf{R}_{s'})} \\
&\quad \times \left[\frac{3\alpha}{a^2} \sum_{s=2}^N (X_s - X_{s-1})(Y_s - Y_{s-1}) \right. \\
&\quad \left. + \beta \sum_{s'=1}^N \Delta U_{s'}(\mathbf{R}_{s'}) \right] d\mathbf{R}_1 \cdots d\mathbf{R}_N, \tag{A7}
\end{aligned}$$

where we have used that $\ln(1 + \Delta) = \Delta$ for small Δ .

Following a similar procedure and taking into account Eq. (8) we find for the deviation of the second part of the ideal free energy in Eq. (5) (notice that there is no contribution from $1/\beta \ln n$!)

$$\begin{aligned}
&-\sum_I \int_{V'} \tilde{U}_I(\mathbf{r}') \tilde{\rho}_I(\mathbf{r}') d\mathbf{r}' + \sum_I \int_V U_I(\mathbf{r}) \rho_I(\mathbf{r}) d\mathbf{r} \\
&= -\sum_I \int_V \Delta U_I(\mathbf{r}) \rho_I(\mathbf{r}) d\mathbf{r} \\
&= -\frac{n\mathcal{N}}{\Phi} \sum_I \int_V \Delta U_I(\mathbf{r}) \sum_{s'=1}^N \delta_{Is'}^K \int_{V^N} \delta(\mathbf{r} - \mathbf{R}_{s'}) \\
&\quad \times e^{-(3/(2a^2)) \sum_{s=2}^N (\mathbf{R}_s - \mathbf{R}_{s-1})^2 - \beta \sum_{s''=1}^N U_{s''}(\mathbf{R}_{s''})} \\
&\quad \times d\mathbf{R}_1 \cdots d\mathbf{R}_N d\mathbf{r} \\
&= -\frac{n\mathcal{N}}{\Phi} \int_{V^N} \sum_{s'=1}^N \Delta U_{s'}(\mathbf{R}_{s'}) \\
&\quad \times e^{-(3/(2a^2)) \sum_{s=2}^N (\mathbf{R}_s - \mathbf{R}_{s-1})^2 - \beta \sum_{s''=1}^N U_{s''}(\mathbf{R}_{s''})} d\mathbf{R}_1 \cdots d\mathbf{R}_N. \tag{A8}
\end{aligned}$$

This result exactly cancels the second term in Eq. (A7). Hence, for small deformations, the principle of virtual work applied to the ideal free energy leads to

$$\begin{aligned}
\delta F^{\text{id}} &= \frac{n\mathcal{N}}{\beta\Phi} \int_{V^N} e^{-(3/(2a^2)) \sum_{s=2}^N (\mathbf{R}_s - \mathbf{R}_{s-1})^2 - \beta \sum_{s'=1}^N U_{s'}(\mathbf{R}_{s'})} \\
&\quad \times \frac{3\alpha}{a^2} \sum_{s=2}^N (X_s - X_{s-1})(Y_s - Y_{s-1}) d\mathbf{R}_1 \cdots d\mathbf{R}_N \\
&= \frac{3n\alpha}{a^2\beta} \left\langle \sum_{s=2}^N (X_s - X_{s-1})(Y_s - Y_{s-1}) \right\rangle. \tag{A9}
\end{aligned}$$

Here, the ensemble average $\langle \rangle$ is taken with respect to the Boltzmann weight $\exp(-(3/(2a^2)) \sum_{s=2}^N (\mathbf{R}_s - \mathbf{R}_{s-1})^2 - \beta \sum_{s'=1}^N U_{s'}(\mathbf{R}_{s'}))$.

APPENDIX B: VIRTUAL WORK PRINCIPLE: DERIVATION OF THE DIAGONAL COMPONENTS OF THE STRESS TENSOR

We now use that

$$\tilde{\rho}_I(x', y', z') = \tilde{\rho}_I((1 + \alpha)x, y, z) = \frac{1}{1 + \alpha} \rho_I(x, y, z), \quad (\text{B1})$$

$$\begin{aligned} \tilde{U}_I(x', y', z') &= \tilde{U}_I((1 + \alpha)x, y, z) \\ &\equiv U_I(x, y, z) + \Delta U_I(x, y, z), \end{aligned} \quad (\text{B2})$$

and also for small α

$$(\mathbf{r}'_1 - \mathbf{r}'_2)^2 = (\mathbf{r}_1 - \mathbf{r}_2)^2 + 2\alpha(x_1 - x_2)^2. \quad (\text{B3})$$

Notice that the deviation $\Delta U_I(x, y, z)$ is different from the deviation we used in deriving the non-diagonal components of the stress tensor. The deformation under consideration now changes the volume; the volume element $dx' dy' dz'$ is equal to $(1 + \alpha) dx dy dz$.

In this case we get both an excluded volume and a cohesive interaction contribution from the non-ideal free energy to σ_{xx}

$$\begin{aligned} \delta F^{\text{nid}} &= -\frac{3\alpha}{2a^2} \sum_{IJ} \int_V \int_V \epsilon_{IJ}(|\mathbf{r}_1 - \mathbf{r}_2|) (x_1 - x_2)^2 \\ &\quad \times \rho_I(\mathbf{r}_1) \rho_J(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 \\ &\quad - \frac{\alpha}{\beta} \sum_I \int_V \rho_I(\mathbf{r}) \frac{(\sum_I v_I \rho_I(\mathbf{r}))^{1/3}}{1 - (\sum_I v_I \rho_I(\mathbf{r}))^{1/3}} d\mathbf{r}. \end{aligned} \quad (\text{B4})$$

Similarly, the ideal free energy now gives a contribution from the connectivity of the chains *and* an ideal gas contribution

$$\delta F^{\text{id}} = -\frac{nN\alpha}{\beta} + \frac{3n\alpha}{a^2\beta} \left\langle \sum_{s=2}^N (X_s - X_{s-1})^2 \right\rangle. \quad (\text{B5})$$

APPENDIX C: THERMODYNAMIC PRESSURE DEFINITION

Notice that definition (26) implies a constant amount of species I and constant temperature T in a copolymer melt.

The ideal part of the thermodynamic pressure is given by:

$$\begin{aligned} p^{\text{t,id}} &= - \left(\frac{\partial F^{\text{id}}}{\partial V} \right)_{nN_I, T} \\ &= - \frac{\partial}{\partial V} \left(-\frac{n}{\beta} \ln \Phi + \frac{1}{\beta} \ln n! - \sum_I \int_V U_I(\mathbf{r}) \rho_I(\mathbf{r}) d\mathbf{r} \right)_{nN_I, T} \\ &= \frac{n}{\beta \Phi} \left(\frac{\partial \Phi}{\partial V} \right)_{nN_I, T} + \sum_I \frac{\partial}{\partial V} \left(\int_V U_I(\mathbf{r}) \rho_I(\mathbf{r}) d\mathbf{r} \right)_{nN_I, T}. \end{aligned} \quad (\text{C1})$$

We apply the following coordinate transformation, which is also used in deriving the virial equation^{70,71}

$$\begin{aligned} x &= V^{1/3} \tilde{x}, \\ y &= V^{1/3} \tilde{y}, \\ z &= V^{1/3} \tilde{z}. \end{aligned} \quad (\text{C2})$$

Now $\tilde{x}$, $\tilde{y}$ and $\tilde{z}$ are volume-independent and the integration limits are set to 0 and 1 (valid for a cube). However, the reduced volume may have any shape. Furthermore, since the total amount of species I is conserved, $V \rho_I(V^{1/3} \tilde{x}, V^{1/3} \tilde{y}, V^{1/3} \tilde{z}) \equiv \tilde{\rho}_I(\tilde{x}, \tilde{y}, \tilde{z})$ is independent of the volume for infinitesimal volume changes which retain the structure in the melt. Hence:

$$\begin{aligned} p^{\text{t,id}} &= \frac{n}{\beta \Phi} \left(\frac{\partial \Phi}{\partial V} \right)_{nN_I, T} + \sum_I \frac{\partial}{\partial V} \left(\int_0^1 \int_0^1 \int_0^1 U_I(V^{1/3} \tilde{x}, V^{1/3} \tilde{y}, V^{1/3} \tilde{z}) \tilde{\rho}_I(\tilde{x}, \tilde{y}, \tilde{z}) d\tilde{x} d\tilde{y} d\tilde{z} \right)_{nN_I, T} \\ &= \frac{nN}{\beta V} - n \frac{\int_V V e^{-(3/(2a^2)) \sum_{s=2}^N (\mathbf{R}_s - \mathbf{R}_{s-1})^2 - \beta \sum_{s'=1}^N U_{s'}(\mathbf{R}_{s'})} (1/(V\beta a^2)) \sum_{s''=2}^N (\mathbf{R}_{s''} - \mathbf{R}_{s''-1})^2 d\mathbf{R}_1 \cdots d\mathbf{R}_N}{\int_V V e^{-(3/(2a^2)) \sum_{s=2}^N (\mathbf{R}_s - \mathbf{R}_{s-1})^2 - \beta \sum_{s'=1}^N U_{s'}(\mathbf{R}_{s'})} d\mathbf{R}_1 \cdots d\mathbf{R}_N} \\ &\quad - n \frac{\int_V V e^{-(3/(2a^2)) \sum_{s=2}^N (\mathbf{R}_s - \mathbf{R}_{s-1})^2 - \beta \sum_{s'=1}^N U_{s'}(\mathbf{R}_{s'})} \sum_{s''=1}^N \partial U_{s''}(\mathbf{R}_{s''}) / \partial V d\mathbf{R}_1 \cdots d\mathbf{R}_N}{\int_V V e^{-(3/(2a^2)) \sum_{s=2}^N (\mathbf{R}_s - \mathbf{R}_{s-1})^2 - \beta \sum_{s'=1}^N U_{s'}(\mathbf{R}_{s'})} d\mathbf{R}_1 \cdots d\mathbf{R}_N} \\ &\quad + n \frac{\sum_{s'=1}^N \delta_{Is'}^K \int_V V e^{-(3/(2a^2)) \sum_{s=2}^N (\mathbf{R}_s - \mathbf{R}_{s-1})^2 - \beta \sum_{s''=1}^N U_{s''}(\mathbf{R}_{s''})} \sum_I \partial U_I(\mathbf{r}) / \partial V e^{-(3/(2a^2)) \sum_{s=2}^N (\mathbf{R}_s - \mathbf{R}_{s-1})^2 - \beta \sum_{s''=1}^N U_{s''}(\mathbf{R}_{s''})} d\mathbf{R}_1 \cdots d\mathbf{R}_N d\mathbf{r}}{\int_V V e^{-(3/(2a^2)) \sum_{s=2}^N (\mathbf{R}_s - \mathbf{R}_{s-1})^2 - \beta \sum_{s'=1}^N U_{s'}(\mathbf{R}_{s'})} d\mathbf{R}_1 \cdots d\mathbf{R}_N} \\ &= \frac{nN}{\beta V} - \frac{2n}{3V} \langle H^G \rangle. \end{aligned} \quad (\text{C3})$$

We have not explicitly written out all coordinate transformations. Notice that the last two terms in Eq. (C3) cancel. The non-ideal part of the pressure can be calculated in a similar way which results in the following expression for the pressure in an inhomogeneous copolymer melt:

$$p^t = \frac{nN}{\beta V} - \frac{2n}{3V} \langle H^G \rangle + \frac{1}{2Va^2} \int_{V^2} \sum_{IJ} \epsilon_{IJ}(|\mathbf{r}-\mathbf{r}'|) \times (\mathbf{r}-\mathbf{r}')^2 \rho_I(\mathbf{r}) \rho_J(\mathbf{r}') d\mathbf{r} d\mathbf{r}' + \frac{1}{\beta V} \sum_I \int_V \rho_I(\mathbf{r}) \frac{(\sum_I \nu_I \rho_I(\mathbf{r}))^{1/3}}{1 - (\sum_I \nu_I \rho_I(\mathbf{r}))^{1/3}} d\mathbf{r}. \quad (\text{C4})$$

If we now compare Eqs. (23) and (C4) we see that indeed $-\frac{1}{3}(\sigma_{xx} + \sigma_{yy} + \sigma_{zz}) = p^t$ as expected.

APPENDIX D: STENCIL OPERATORS

We define a stencil operator for numerically evaluating

$$\xi[f](\mathbf{r}) \equiv \frac{1}{a^2} \left(\frac{3}{2\pi a^2} \right)^{3/2} \int_V e^{-(3/(2a^2))(\mathbf{r}-\mathbf{r}')^2} \times (\mathbf{r}-\mathbf{r}')^2 f(\mathbf{r}') d\mathbf{r}', \quad (\text{D1})$$

with Fourier transform

$$(\xi_{\mathbf{q}} f_{\mathbf{q}})_{\text{cont}} \equiv \left(1 - \frac{a^2 \mathbf{q}^2}{9} \right) e^{-a^2 \mathbf{q}^2/6} f_{\mathbf{q}}. \quad (\text{D2})$$

The Fourier transformed stencil operator is given by:⁶⁴

$$(\xi_{\mathbf{q}})_{\text{disc}} \equiv c_0 + c_1 [\cos(q_x h) + \cos(q_y h) + \cos(q_z h)] + c_2 [\cos(q_x h - q_y h) + \cos(q_x h + q_y h) + \cos(q_x h - q_z h) + \cos(q_x h + q_z h) + \cos(q_y h - q_z h) + \cos(q_y h + q_z h)] + c_3 [\cos(q_x h - q_y h - q_z h) + \cos(q_x h + q_y h - q_z h) + \cos(q_x h - q_y h + q_z h) + \cos(q_x h + q_y h + q_z h)]. \quad (\text{D3})$$

We now have 5 degrees of freedom (c_0, c_1, c_2, c_3 and a/h) which are determined by fitting the discrete stencil operator $(\xi_{\mathbf{q}})_{\text{disc}}$ and the continuous operator $(\xi_{\mathbf{q}})_{\text{cont}}$ to each other in the points $(0,0,0)$, $(\pi/h, 0, 0)$, $(\pi/h, \pi/h, 0)$, $(\pi/h, \pi/h, \pi/h)$ and $(\pi/2h, \pi/2h, \pi/2h)$ in Fourier space. Notice that $(\pi/h, \pi/h, \pi/h)$ is the maximum frequency that is represented on the grid. This results in:

$$\begin{aligned} c_0 &= 0.108833, \\ c_1 &= 0.137502, \\ c_2 &= 0.0628806, \\ c_3 &= 0.0253439, \\ \frac{a}{h} &= 0.91758. \end{aligned} \quad (\text{D4})$$

Other fit procedures result in less accuracy over the entire frequency range. Unfortunately, the ratio a/h now differs from the optimum value $a/h = 1.15430$ that resulted from accurately trying to evaluate Eq. (29). Also, the user is free to choose a value for a/h , which will, from the viewpoint of computational efficiency, most likely be smaller than 1.15430. Therefore, we have studied optimal discrete stencil operators for values of $a/h = 1.15430$ and $a/h = 1.26973$ (10% higher). Notice that $a/h = 0.91758$ is already more than 20% below the optimal value. We found that fitting the discrete and continuous operators to each other in the points $(0,0,0)$, $(\pi/h, 0, 0)$, $(\pi/h, \pi/h, 0)$ and $(\pi/h, \pi/h, \pi/h)$ results in general in an accurate representation. The optimal values for the stencil coefficients are in these cases given by:

a	1.15430	1.26973
$\frac{a}{h}$		
c_0	0.0960917	0.0997763
c_1	0.122149	0.119996
c_2	0.0669248	0.0665782
c_3	0.0339781	0.0351918

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