

A hierarchical model for surface effects on chain conformation and rheology of polymer solutions. I. General formulation

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The flow behavior of polymer solutions near a solid surface (either neutral or adsorbing) is modeled through a new, hierarchical (macroscopic and microscopic) approach which enables the thermodynamically consistent extension of equilibrium (static) considerations to nonequilibrium (flow) conditions. The approach involves two steps: First, the set of primary, independent, variables defining the state of the system at the macroscopic level is chosen, and a complete set of transport and constitutive equations is constructed for them through a two fluid, Hamiltonian model. In the present work, the macroscopic variables include the polymer chain concentration, the macroscopic fluid velocity, and the conformation tensor (defined as the tensor of the second moment of the chain end-to-end vector). The governing equations involve the (extended) free energy or Hamiltonian of the system, H , and are valid both in the bulk of the fluid and in the interfacial region. Thus, to solve them one needs to specify H . This is done in a second step, by invoking a microscopic model, which consistently takes into account the simultaneous effect on chain conformations of both the solid boundary and the imposed flow field. Solid boundary effects are taken into account in the solution of a diffusion equation for the chain propagator $G(\mathbf{r}, n; \mathbf{r}_0)$ which represents the weighted probability that an n -segment long chain which starts at \mathbf{r}_0 will end at position \mathbf{r} . Flow field effects are taken into account through the definition of a generalized propagator $G'(\mathbf{r}, n; \mathbf{r}_0, \boldsymbol{\alpha})$, which further depends on the apparent strain tensor $\boldsymbol{\alpha}$, representing chain deformation effects due to flow. The present part of the paper describes the general formulation of the approach and its relevance with previous works. Results from applying the methodology to the case of a polymer solution flowing past a purely repulsive surface (a wall) are presented in the second part of this work.

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I. INTRODUCTION

The study of the behavior of polymer solutions next to solid surfaces has received a great deal of attention in the past few years,^{1–6} not only because of its intrinsic scientific interest but also because of its technological importance. We can mention the role of adsorbed polymer molecules in the stability of colloidal suspensions against flocculation, their use as adhesives and lubricants, and the significance of polymer-wall interactions in polymer flows through porous media.^{7–9} In most of these cases, the interaction of polymer molecules with the solid surface takes place under the application of an external flow field. The flow field deforms the polymer molecules and further enhances the conformational changes in the interfacial region. Better understanding of this fundamental interplay between flow and surface effects on the structure and conformational properties of polymer molecules can, therefore, significantly improve our capability for designing more efficient interfacial systems tailored for specific use in particular applications.

So far, most of the existing studies of polymer–surface

interactions have focused on the (static) equilibrium problem,^{1,2,5,6} where a fairly good understanding has been developed; on the contrary, very few works have undertaken the same problem under flow conditions.^{3,4} The lack of an adequate analysis for the flow problem can be attributed to the inherent complexity of the system, but also to the lack of a consistent thermodynamic and mathematical formalism that could enable the consistent extension and utilization of equilibrium concepts and principles to the nonequilibrium (flow) regime. We use here the recently developed Hamiltonian formalism of dissipative flow processes in media with internal microstructure^{10–12} in order to systematically investigate the combined effects of the adjacency to a solid surface and the imposed flow field on the polymer concentration and conformation.

The development of a Hamiltonian formalism for dissipative systems started with the pioneering works of Kaufman, Morrison, and Grmela which all appeared almost simultaneously in 1984.^{13–15} After that, significant research activity followed in the field which eventually culminated to more systematic and broad descriptions such as the generalized bracket¹¹ and, more recently, the GENERIC formalisms.¹⁶ These latest two formalisms have proven to be equivalent in all but the Boltzmann equation (which can only be described by the GENERIC formalism).^{16,17} The key underlying assumption of the Hamiltonian approach is the ex-

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istence of a partial (local) thermodynamic equilibrium, which can be described by only a few internal variables (such as the second moment of the distribution function for the polymer end-to-end distance vector), in addition to the traditional and widely used thermodynamic variables, like the density and the temperature. In the following we employ the methodology developed within the generalized bracket formalism as described in our previous work.^{11,12}

So far, the Hamiltonian approach has enabled the description of the dynamics of many polymer flowing systems.^{11–16} In simple test cases, it has duly led to the same transport equations as the ones obtained from the application of more conventional conservation and continuum mechanics principles. In more complicated cases, it has allowed for the evaluation of the thermodynamic consistency of various proposed models. In such cases, it needs to be coupled with an analysis of the microscopic physics in order to give more valuable results. It is this combination of the microscopic modeling of the system internal structure with the macroscopic Hamiltonian formalism that provides a means for studying the interaction of the (microscopic) polymer chain conformations with a (macroscopic) flow in the adjacency of a solid surface.

In fact, this approach has already been followed in a previous publication,¹⁸ in connection with the assumption of a Gaussian distribution function for the chain end-to-end distance vector, in order to give a qualitative description of the effects of a purely repulsive surface (a solid wall) on the conformation, concentration, and rheology of a dilute polymer solution in a simple shear flow. Compared to that previous work,¹⁸ in the present study, the length scale of analysis of the microscopic deformations is reduced from distances commensurate with the average end-to-end chain length (which is the minimum length scale for which the previously assumed Gaussian approximation is valid) to distances commensurate with the length of the repeat (polymer segment) unit. This refinement is made possible through the use of a self-consistent mean-field approach, based on the random flight chain model, describing chain conformations under an externally imposed field.

This paper is the first in a series of two. It presents the general formalism valid under both equilibrium and nonequilibrium (flow) conditions, and makes the connection with previously developed theoretical works. It is organized as follows: Section II presents the macroscopic governing equations in their most general form, valid under both static (equilibrium) and dynamic (flow) conditions. Section III describes the relevant terms entering into the expression for the extended free energy of the system; the microscopic model and the quantities it utilizes are described here in great detail. Section IV follows with some additional calculations needed to evaluate a number of important mathematical quantities. In Sec. V, we give a description of the algorithm that should be followed for the solution of the combined microscopic–macroscopic equations. Finally, in Sec. VI, we present our conclusions.

II. MACROSCOPIC FORMALISM: GOVERNING EQUATIONS IN TERMS OF A FREE ENERGY FUNCTIONAL

The analysis of surface–polymer interactions is based on a consistent modification of the expression for the extended free energy of the system that enters into a set of continuum equations governing the rheology and mass transfer phenomena in dilute polymer solutions at the macroscopic level. These equations represent an extension of the traditional transport equations for fluids characterized by an internal microstructure. The effect of microstructure is taken into account through the extra stress or conformation tensor, and in the evaluation of the extended free energy of the system upon which these equations depend. Similar equations have been derived by a number of researchers: Helfand and Fredrickson¹⁹ and Milner²⁰ coupled the internal deformation state with the number density of the polymer molecules in the description of the rheology and mass transfer. In parallel, Doi,²¹ Onuki,²² and Bhawe *et al.*²³ arrived independently at similar sets of equations describing stress-induced concentration and conformation changes in flows of dilute polymer solutions, where the polymer molecules were modeled as linearly elastic “Hookean” dumbbells. The same problem has also been addressed from a continuum viewpoint by Öttinger²⁴ and more recently by Mavrantzas and Beris²⁵ based on a two-fluid model. Although all of these approaches have resulted into similar sets of equations, subtle differences exist among them, which, as was shown in a recent publication,²⁶ can prove critical in our capability to carry out computations.

The investigation of the differences between the equations derived from three different formalisms, the body-tensor,²⁴ the two-fluid Hamiltonian,²⁵ and an inhomogeneous kinetic theory,²³ was undertaken in a recent publication.²⁷ There it was shown that, if all relevant terms in the inhomogeneous kinetic theory analysis are consistently taken into account, the resulting equations are in perfect agreement with those of the two continuum theories, at least up to the leading order term in an expansion of the solution variables with respect to their equilibrium values.²⁷ The consistent application of the kinetic theory to inhomogeneous flows has also been the subject of a very recent paper by Curtiss and Bird.²⁸ Their findings further reinforce the conclusions of Beris and Mavrantzas²⁷ (see, in particular, their Appendix B), as they consistently extend the inhomogeneous kinetic theory analysis to a broader class of macromolecular models. In the following, our two-fluid formulation²⁵ is used as the basis for the modeling of surface interactions, since it is the one involving the fewest parameters, while simultaneously yielding consistent results for a variety of inhomogeneous rotating viscometric flows,²⁶ as compared against previous investigations.^{3,4,29,30}

The main assumption behind the two-fluid model is that of two interpenetrating continua corresponding to the polymer and solvent molecules, which are assumed to be in thermal but not mechanical equilibrium. Then, for an incompressible dilute polymer solution, the governing equations are derived as follows—for a detailed analysis see Chap. 9.2.2 of Ref. 11 and Chap. 2 of Ref. 31. The two phases of

the system are assumed to be completely characterized by the following set of primary (independent) variables: The total mass density ρ , taken to be constant for an incompressible system considered here, corresponding to a total segment (polymer plus solvent) number density ρ_0 , the polymer chain fraction number, n_1 , the total momentum density $\mathbf{M} = \rho \mathbf{v}$, where \mathbf{v} is the total velocity field, and an internal structural parameter, $\mathbf{C} = \rho_0 n_1 \mathbf{c}$, where \mathbf{c} is a second-order tensor characterizing the conformation of polymer molecules. For an isolated Rouse chain in the bulk, \mathbf{c} can be identified with the second moment of the distribution function for the end-to-end distance vector of the polymer chains. Of course, more detailed internal structural parameters, of discrete (such as the moments of the intrabead position vectors of a Rouse chain³²) or even continuum (such as a distribution function^{33,34}) nature can also be introduced into the description of the internal microstructure. However, this is accomplished at the expense of complexity, thus, prohibitively increasing the applicability of the model. Since these results can usually be closely followed up with suitable closure approximations,³⁴ this path is not pursued any further in the present work.

We assume that the system is characterized by an extended free energy functional, H , which is the sum of the kinetic energy, H_k , and an internal free energy part, H_i :

$$H \equiv H_k + H_i = \int [h_k(y) + h_i(y)] A \, dy, \quad (1)$$

where $h_k = \rho v^2/2$ is the kinetic energy density, h_i is the internal free energy density, A stands for the surface area in the plane (x - z), and y is the component perpendicular to the surface; h_i is, in general, considered to be a function of all: n_1 , \mathbf{C} , and the position vector \mathbf{r} . Although the use of coarse-grained, structural parameters, such as the conformation tensor \mathbf{C} or \mathbf{c} , describing the overall polymer conformation in an average sense, as independent arguments of the free energy density function is not an entirely new idea in irreversible thermodynamics approaches to melt viscoelasticity, it is only during the last years that people in polymer community have started using it. For example, very recently, Mavrantzas and Theodorou³⁵ used it, in conjunction with an atomistic simulation of a polymer melt, to calculate the free energy of an oriented polyethylene melt.

In general, in order to represent spatial inhomogeneities within the system, gradients of the primary variables need also to be included among the arguments of h_i , as was very convincingly shown in the influential pioneering work by Helfand,³⁶ followed later by many others.³⁷ Alternatively, one can describe inhomogeneous effects through the dependence of the Hamiltonian density on some auxiliary variables, connected to the primary variables through nonlocal (integral) relations. Such an auxiliary variable, widely used in the present application, is the segment density φ . In this way, inhomogeneous entropic effects are captured by the chain partition function Z [first term on the right-hand-side of Eq. (18) below] exactly as was done by Hong and Noolandi³⁷ (see their Eq. 2-20), representing the relative number of chain conformations in the interfacial region relative to the bulk. Such entropic effects usually dominate in the

high molecular weight polymer regime (Helfand regime, Fredrickson³⁸), which is exactly the regime that we are interested in describing here. Thus, although, an explicit dependence of H also on gradients of the primary variables is possible within the formalism adopted here [see, for example, Eq. 5.2-6 in the monograph by Beris and Edwards¹¹], such a dependence will be neglected in the present study, just only in order to simplify the mathematics and keep the complexity of model equations at a low, tractable level.

In our two-fluid Hamiltonian model, the starting point is that of the notion of two interpenetrating, but noninteracting continua which we label as (1) and (2). Component (2) is assumed to be structureless, whereas component (1) is assumed to be viscoelastic, characterized by a structural parameter, the conformation tensor \mathbf{C} . According to the Hamiltonian approach¹¹ followed in this work, the governing equations are obtained from the dynamic equations developed for an arbitrary functional F :

$$\frac{dF}{dt} = \{F, H\} + [F, H], \quad (2)$$

after the Poisson bracket $\{F, G\}$ and the dissipative bracket $[F, G]$ have been defined for arbitrary functionals F and G . In this work, the Poisson bracket is taken to have two contributions

$$\{F, G\} = \{F, G\}_1 + \{F, G\}_2. \quad (3)$$

The first contribution $\{F, G\}_1$ involves the direct sum of the terms corresponding to two interpenetrating continua each one taken as a single compressible fluid written (following, for example, Morrison and Greene³⁹) in terms of the individual mass and momentum densities, (ρ_1, \mathbf{m}_1) and (ρ_2, \mathbf{m}_2) , respectively,

$$\begin{aligned} \{F, G\}_1 = \int & \left(- \left[\frac{\delta F}{\delta \rho_1} \nabla_\beta \left(\frac{\delta G}{\delta m_\beta^1} \right) - \frac{\delta G}{\delta \rho_1} \nabla_\beta \left(\frac{\delta F}{\delta m_\beta^1} \rho_1 \right) \right] \right. \\ & - \left[\frac{\delta F}{\delta \rho_2} \nabla_\beta \left(\frac{\delta G}{\delta m_\beta^2} \right) - \frac{\delta G}{\delta \rho_2} \nabla_\beta \left(\frac{\delta F}{\delta m_\beta^2} \rho_2 \right) \right] \\ & - \left[\frac{\delta F}{\delta m_\alpha^1} \nabla_\beta \left(\frac{\delta G}{\delta m_\beta^1} m_\alpha^1 \right) - \frac{\delta G}{\delta m_\alpha^1} \nabla_\beta \left(\frac{\delta F}{\delta m_\beta^1} m_\alpha^1 \right) \right] \\ & \left. - \left[\frac{\delta F}{\delta m_\alpha^2} \nabla_\beta \left(\frac{\delta G}{\delta m_\beta^2} m_\alpha^2 \right) - \frac{\delta G}{\delta m_\alpha^2} \nabla_\beta \left(\frac{\delta F}{\delta m_\beta^2} m_\alpha^2 \right) \right] \right) dV, \end{aligned} \quad (4)$$

where $\mathbf{m}_1 = \rho_1 \mathbf{u}_1$ and $\mathbf{m}_2 = \rho_2 \mathbf{u}_2$ are the momentum densities of the two fluids. The second term $\{F, G\}_2$ involves elastic contributions and refers to the viscoelastic component (component 1), characterized by the internal structural parameter \mathbf{C} , i.e., the conformation tensor

$$\begin{aligned} \{F, G\}_2 = & \int \left(- \left[\frac{\delta F}{\delta C_{\alpha\beta}} \nabla_\gamma \left(\frac{\delta G}{\delta m_\gamma^T} C_{\alpha\beta} \right) \right. \right. \\ & \left. \left. - \frac{\delta G}{\delta C_{\alpha\beta}} \nabla_\gamma \left(\frac{\delta F}{\delta m_\gamma^T} C_{\alpha\beta} \right) \right] \right. \\ & - C_{\alpha\beta} \left[\nabla_\alpha \left(\frac{\delta F}{\delta m_\gamma^T} \right) \frac{\delta G}{\delta C_{\gamma\beta}} - \nabla_\alpha \left(\frac{\delta G}{\delta m_\gamma^T} \right) \frac{\delta F}{\delta C_{\gamma\beta}} \right] \\ & \left. - C_{\alpha\beta} \left[\nabla_\beta \left(\frac{\delta F}{\delta m_\gamma^T} \right) \frac{\delta G}{\delta C_{\gamma\alpha}} - \nabla_\beta \left(\frac{\delta G}{\delta m_\gamma^T} \right) \frac{\delta F}{\delta C_{\gamma\alpha}} \right] \right) dV. \end{aligned} \quad (5)$$

The above form originated from Marsden *et al.*⁴⁰ and, for an elastic medium, it was exactly derived by Edwards and Beris⁴¹ from first principles.

Next, we derive the continuity and the momentum balance equations for the two individual species and the evolution equation for the conformation tensor \mathbf{C} solely based on the reversible dynamics described by the above well-established Poisson brackets, through a direct comparison of the dynamic Eq. (2) with the chain rule of differentiation applied to an arbitrary functional F .¹¹ Then, two new sets of variables are introduced, the total mass density ρ with its corresponding momentum density \mathbf{M} , and the reduced mass density ρ_- with its corresponding momentum density \mathbf{M}_- , i.e., (ρ, \mathbf{M}) and (ρ_-, \mathbf{M}_-) :

$$\begin{aligned} \rho &= \rho_1 + \rho_2, \quad \mathbf{M} = \mathbf{m}_1 + \mathbf{m}_2, \\ \rho_- &= \rho_1, \quad \mathbf{M}_- = \frac{\rho_2}{\rho_1 + \rho_2} \mathbf{m}_1 - \frac{\rho_1}{\rho_1 + \rho_2} \mathbf{m}_2. \end{aligned} \quad (6)$$

The velocities \mathbf{v} and $\Delta \mathbf{v}$ that the two new momentum densities refer to are

$$\begin{aligned} \mathbf{v} &\equiv \frac{\mathbf{M}}{\rho_1 + \rho_2} = \frac{\rho_1}{\rho_1 + \rho_2} \mathbf{u}_1 + \frac{\rho_2}{\rho_1 + \rho_2} \mathbf{u}_2, \\ \Delta \mathbf{v} &\equiv \frac{\mathbf{M}_-}{\rho_-} = \mathbf{u}_1 - \mathbf{u}_2, \end{aligned} \quad (7)$$

respectively. In this way, the incompressibility constraint is easily taken into account by imposing

$$\nabla \cdot \mathbf{M} = 0 \Leftrightarrow \nabla \cdot \mathbf{v} = 0, \quad (8)$$

in the final equations, where \mathbf{v} represents the mass average velocity of the mixture.

So far the two components of the fluid have been assumed noninteracting. Thus, the dissipative bracket $[F, G]$ is next introduced, which involves three terms: The first is a viscous term, the second is a drag contribution term due to the fact that the two components in the mixture are allowed to move with different, in general, velocities and the third is a relaxation term for the polymer viscoelasticity

$$\begin{aligned} [F, G] = & - \int \frac{\eta_s}{2} \left[\nabla_\alpha \frac{\delta F}{\delta M_\beta} + \nabla_\beta \frac{\delta F}{\delta M_\alpha} \right] \left[\nabla_\alpha \frac{\delta G}{\delta M_\beta} \right. \\ & \left. + \nabla_\beta \frac{\delta G}{\delta M_\alpha} \right] dV - \int Z_{\alpha\beta} \frac{\delta F}{\delta M_{-\alpha}} \frac{\delta G}{\delta M_{-\beta}} dV \\ & - \int \frac{2}{\lambda \rho_0 n_1 K} C_{\alpha\beta} \frac{\delta F}{\delta C_{\alpha\gamma}} \frac{\delta G}{\delta C_{\beta\gamma}} dV, \end{aligned} \quad (9)$$

plus their corresponding entropy correction terms which do not need to be mentioned, since they only affect nonisothermal processes. These are the only phenomenological dissipative interactions assumed in our model, and they correspond to well-established quadratic terms for the entropy production allowed in the system, representing the lowest order of a more general nonlinear dissipation. In the above equation, η_s is the solvent viscosity, which is constrained to be non-negative, Z is the drag coefficient tensor, which is assumed to be symmetric and positive definite, λ is the polymer relaxation time, and K the Hookean spring constant. The dissipative form of the evolution equations can then be obtained by evaluating the additional terms arising from the introduction of the dissipative bracket into the dynamic equation for an arbitrary functional F , Eq. (2). Note that exactly the same form of the equations would have been derived based on the more recently formulated GENERIC approach¹⁶ given the equivalence of the two approaches as demonstrated in several occasions,^{16,17} also covering the present macroscopic model.

By re-expressing the resulting equations in terms of the new sets of variables (ρ, \mathbf{M}) and (ρ_-, \mathbf{M}_-) and neglecting inertial terms, a linear equation is obtained for $\Delta \mathbf{v}$. If this is solved for $\Delta \mathbf{v}$ and substituted back into the equation for \mathbf{M} , a one-fluid reduction of the two-fluid model can be obtained. This consists of three equations: The momentum equation for the total mass density, the evolution equation for the conformation tensor, and the conservation or diffusion equation for the density of the viscoelastic component, component (1), with a diffusivity tensor \mathbf{Y} given by

$$\mathbf{Y} = \rho_1 \left(1 - \frac{\rho_1}{\rho_1 + \rho_2} \right)^2 \mathbf{Z}^{-1}. \quad (10)$$

For a steady-state unidirectional flow, where the velocity field has only one component, v_x , in the direction x , varying only along the perpendicular direction y , i.e., $v_x = v_x(y)$, the substantial derivatives of all variables of interest with respect to time are zero, and the final macroscopic governing equations that are obtained are as follows.^{11,27,41}

The first is the momentum equation

$$0 = -\nabla p + \eta_s \nabla^2 \mathbf{v} + \nabla \cdot \boldsymbol{\sigma} - \nabla \Pi - \frac{\partial h_i}{\partial \mathbf{r}}, \quad (11)$$

the second is the constitutive equation

$$\mathbf{C}_{(1)} = -\frac{1}{\lambda K} \boldsymbol{\sigma}, \quad (12)$$

where the subscript (1) denotes the upper-convected time derivative

$$\mathbf{C}_{(1)} \equiv \frac{\partial \mathbf{C}}{\partial t} + \mathbf{v} \cdot \nabla \mathbf{C} - \mathbf{C} \cdot \nabla \mathbf{v} - \nabla \mathbf{v}^T \cdot \mathbf{C}, \quad (13)$$

and the third is the concentration equation

$$0 = \nabla \cdot \left[\mathbf{Y} \cdot \left(\nabla \Pi + \frac{\partial h_i}{\partial \mathbf{r}} - \nabla \cdot \boldsymbol{\sigma} \right) \right]. \quad (14)$$

Equation (11) is the momentum equation for the total velocity field. This is seen to involve into the right-hand-side, in addition to the traditional pressure and viscous terms (p is the pressure and η_s the solvent viscosity), three extra terms: The first is a polymer contribution to the stress, $\boldsymbol{\sigma}$, defined as

$$\boldsymbol{\sigma} \equiv 2\mathbf{C} \cdot \frac{\delta H}{\delta \mathbf{C}}, \quad (15)$$

the second is a contribution from the osmotic pressure Π , defined as

$$\Pi \equiv n_1 \frac{\delta H_i}{\delta n_1} + \mathbf{C} : \frac{\delta H}{\delta \mathbf{C}} - h_i, \quad (16)$$

and the third is a nonhomogeneous term due to the direct dependence of the internal part of the free energy density h_i on the local position \mathbf{r} . In Eqs. (11) and (14) above and in the following, the partial derivative $\partial/\partial \mathbf{r}$ denotes a direct differentiation with respect to position \mathbf{r} keeping all other variables on which h_i explicitly depends constant; this term is, therefore, zero in homogeneous bulk flows. The same convention holds for the partial derivatives with respect to all other variables. In contrast, the gradient operator ∇ denotes the total derivative with respect to \mathbf{r} including both direct and indirect (through differentiation by parts) contributions, while the symbol $\delta H/\delta a$ denotes the Volterra derivative of the Hamiltonian functional, Eq. (1), with respect to the variable a , $a = n_1$, \mathbf{C} or \mathbf{v} .

Equation (12) is the constitutive equation for the conformation tensor \mathbf{C} which, together with (a) the expression for the extra stress tensor provided by Eq. (15) and (b) the expression for h_i that corresponds to a solution of polymer molecules modeled as infinitely extensible random chains or Hookean dumbbells,¹¹ is equivalent to the upper-convected-Maxwell or Oldroyd-B model. For simplicity, the relaxation time λ is assumed constant in our work, signifying, among other assumptions, a constant mobility. If hydrodynamic interactions are taken into account, this assumption is no longer valid and λ becomes a function, in general, of the conformation tensor.¹¹ However, for systems close to a solid surface, a spatial dependence of the hydrodynamic interaction should also be anticipated. Given the high complexity of the existing model already, such a feature is left to be examined in a future work.

Finally, Eq. (14) is the conservation of mass equation for the polymer species, with \mathbf{Y} representing the diffusivity (assumed constant here) and $\nabla \Pi + \partial h_i/\partial \mathbf{r} - \nabla \cdot \boldsymbol{\sigma}$ an extended driving force. In the absence of a polymer contribution to the stress and for a free energy density, h_i , not dependent on the local position, this equation reduces to the traditional mass diffusion equation, with the osmotic pressure Π then identified with the chemical potential. In fact, as also derived in

other works,^{3,20–24} we immediately notice the presence of the gradient of the polymer excess stress, $\nabla \cdot \boldsymbol{\sigma}$, in the driving force of Eq. (14). This term is responsible for stress-induced polymer migration phenomena, as for example, discussed in Refs. 3 and 23–27. In addition, we notice the presence of the term $\partial h_i/\partial \mathbf{r}$ describing the partial derivative of the free energy density with respect to \mathbf{r} keeping all the other variables constant. As mentioned above, this term is nonzero only if there is a direct dependence of h_i on the local position; therefore, it is zero in the bulk, where the medium is assumed to be homogeneous. However, as we will see in the following, the presence of a solid surface does induce such a dependence, so it is important to keep the corresponding term into the diffusion driving force.

As can be clearly seen from an inspection of the governing equations, they crucially depend on the Hamiltonian H , and in particular on the internal free energy density h_i . Since the relevant physics for the problem is introduced into the model primarily through the specification of h_i , defining h_i is not a trivial issue, and this is separately done in the following section, Sec. III, in conjunction with a microscopic analysis of the chain conformations near the surface.

III. MICROSCOPIC FORMALISM: THE INTERNAL FREE ENERGY DENSITY

Consistently with the mean-field approach followed in this work, the internal free energy density of the polymer solution, h_i , is taken to consist of three contributions

$$h_i = h_{\text{mix}} + h_{\text{surf}} + h_{\text{def}}. \quad (17)$$

The first term, h_{mix} , describes the free energy density due to the random mixing of polymer segments with solvent molecules in the adjacency of a solid surface; it is this term that involves an explicit dependence of the free energy density on \mathbf{r} . The second term, h_{surf} , arises due to possible additional enthalpic interactions of polymers with the solid surface. Finally, the third term, h_{def} , describes the entropic corrections to the free energy arising from the nonequilibrium deformation of the chains due to the imposed flow field.

A. The free energy of random mixing

To the first order, the free energy density of mixing can be approximated by a Flory–Huggins-type equation

$$\frac{h_{\text{mix}}}{\rho_0 k_B T} = n_1(y) \ln \left(\frac{n_1(y)N}{Z(N-1, y)} \right) + (1 - \varphi(y)) \ln(1 - \varphi(y)) + \chi \varphi(y)(1 - \varphi(y)), \quad (18)$$

where n_1 has already been defined as the number fraction of polymer molecules, φ is the number fraction of polymer segments, χ is the Flory-chi parameter, and $Z(N-1, y)$ is the chain partition function, defined immediately below, representing the relative number of conformations of an $N-1$ segment chain starting at y versus the number of conformations for the same chain in the bulk. In the way used above, $Z(N-1, y)$ is exactly the same as the quantity ω_c used by Scheutjens and Fleer⁵ to describe the ratio of the number of arrangements of a chain in conformation c and that of a chain

in the bulk. In fact, Eq. (18) arises as the continuum analog of Eq. (13) of the Scheutjens–Fleer lattice model⁵ where the continuum distance from the wall, y , is used in lieu of the discrete lattice layer index. For example, in the Scheutjens–Fleer formulation, n_c is the number of chains belonging to conformation c , which is represented as $n_1(y)$ here, denoting the number fraction of chains starting at y . Throughout this paper it is assumed that the volumes occupied by a polymer segment and a solvent molecule are equal so that the segment number density is always equal to the volume segment fraction. The case where polymer segments and solvent molecules are assumed to have differing molar volumes has been addressed recently.⁴²

Equation (18) was originally derived by Flory⁴³ for a homogeneous solution where the following relationship between the (constant) segment and (constant) chain number fractions, φ and n_1 , respectively, holds:

$$n_1 = \frac{\varphi}{N} \quad (\text{homogeneous medium}), \quad (19)$$

with N representing the chain length, i.e., the total number of segment links per chain is $N-1$. In the present work, though, we are interested in investigating spatial inhomogeneities in the polymer solution which typically extend down to such small length scales as the segment size. Thus, a consistent generalization of Eq. (19) is needed to close the system of equations. This is achieved by utilizing the chain conformation probabilities, and more precisely the concept of the propagator, as shown immediately below.

First, we need to define a means for counting chains. Although any point within a chain can serve as a reference point, in the present work, we chose the end points. In fact, since either end of a chain can be taken as a reference point, both of them should be treated as equivalent in the analysis, and thus, we take n_1 as $n_{1,e}/2$, where $n_{1,e}$ is the fraction of chain end points, in consistence with lattice model descriptions. We also introduce into the analysis in an *ad hoc* fashion the concept of the propagator. Assuming that the statistics of chains remains Gaussian in the two neutral x and z directions, we focus our attention on the y axis, and we define the propagator $G(y,n;y_0)$ such that $G(y,n;y_0) dy$ is proportional to the number fraction of n -segment chains that start at a distance y_0 above the surface and end at y within dy . To calculate $G(y,n;y_0)$, we can resort to the diffusion equation approach,^{44,45} according to which, if no excluded volume effects are considered, $G(y,n;y_0)$ satisfies

$$\frac{\partial G(y,n;y_0)}{\partial n} = \frac{\ell^2}{6} \frac{\partial^2 G(y,n;y_0)}{\partial y^2}, \quad (20)$$

with initial condition

$$\text{at } n=0, \quad G(y,0;y_0) = \delta(y-y_0), \quad (21)$$

and boundary conditions dictated by the specification of the problem; in Eq. (20), ℓ is the chain segment length.

The proportionality coefficient for $G(y,n;y_0)$ is so selected that the integral of the propagator over all possible chain end locations gives the chain partition function $Z(n,y_0)$:

$$Z(n,y_0) \equiv \int_0^\infty G(y,n;y_0) dy, \quad (22)$$

with its meaning as specified above. Then the number fraction of segments φ is connected with the number fraction of chain ends $n_{1,e}$ as follows:

$$\varphi(y) = \sum_{n=0}^{N-1} \int_0^\infty \frac{1}{2} n_{1,e}(y_0) \times \frac{G(y,n;y_0) \int_0^\infty G(y',N-1-n;y) dy'}{Z(N-1,y_0)} dy_0. \quad (23)$$

In Eq. (23), the integral of $G(y',N-1-n;y)$ over y' ensures that the rest of the $(N-1)$ -segment chain (i.e., of $N-1-n$ segments long) is above the confining boundary, and the denominator is the normalizing constant $Z(N-1,y_0)$, taking into account all possible conformations of the entire $(N-1)$ links long chain that happens to start at y_0 ; further, the factor $\frac{1}{2}$ corrects for double counting the chains through both their end segments. By using Eq. (22), Eq. (23) takes the form

$$\varphi(y) = \sum_{n=0}^{N-1} \int_0^\infty \frac{1}{2} n_{1,e}(y_0) G(y,n;y_0) \frac{Z(N-1-n,y)}{Z(N-1,y_0)} dy_0. \quad (24)$$

Equation (24) is the correct generalization of Eq. (19) for inhomogeneous polymer solutions, and can also be compared against a similar formula proposed by Dolan and Edwards⁴⁶ for chains permanently anchored on a surface [Eq. (6) in their paper]. Indeed, in the limiting case that $n_{1,e}$ is a delta function at the surface, Eq. (24) reduces to their equation. Once $n_{1,e}$ has been determined, other chain density measures can be evaluated; for example, the middle chain density $n_{1,m}$ can be obtained as

$$n_{1,m}(y) = \int_0^\infty \frac{1}{2} n_{1,e}(y_0) \times G\left(y, \frac{N-1}{2}; y_0\right) \frac{Z\left(\frac{N-1}{2}, y\right)}{Z(N-1,y_0)} dy_0. \quad (25)$$

Of particular significance is the quantity $Z(N-1,y_0)$, defined by Eq. (22), because it is the partition function of the corresponding chain whose origin is at y_0 .^{47–49} This quantity is bound to play a central role in the analysis, since it conveys all the information for the effects of the surface on the polymer molecules at the conformational level.

B. Enthalpic surface contributions to the free energy

The second component of the free energy arises from possible enthalpic interactions of polymer molecules with the solid surface. The solid surface directly affects the thermodynamic state of the solution in two ways: First, if the surface is adsorbing, polymer segments gain energy by coming close enough to it. In such a case, since the chains consist of a large number of monomeric units all of which can, in principle, interact with the adsorbing surface, a crowding of the interfacial region in polymer segments is expected, and

segment-segment interactions should be very important, even when the energy of adsorption is very low.

Second, the presence of the solid surface changes the statistics of the polymer conformations in its vicinity; this means that the number of conformations $G(\mathbf{r}, n; \mathbf{r}_0)$ from \mathbf{r}_0 to \mathbf{r} involving n segments depends highly on the distance from the wall of the point of origin \mathbf{r}_0 of the chain. Far away from the wall, of course, chain conformations at the level of approximation of our work are isomorphic to the random flight problem with equal probabilities, and $G(\mathbf{r}, n; \mathbf{r}_0)$ obeys a Gaussian distribution. The above effects influence the total number of available conformations $Z(N-1, y_0)$ defined by Eq. (22), which determines the internal conformational entropy of the system. This entropic effect has already been taken into account in the definition of h_{mix} described in Eq. (18) above.

The expression for the enthalpic contribution of the surface to the free energy, h_{surf} is therefore, written as

$$\frac{h_{\text{surf}}}{\rho_0 k_B T} = u_s - \varphi_s \chi_s \delta(y), \quad (26)$$

where χ_s is the adsorption energy parameter

$$\chi_s = -(u_p - u_s), \quad (27)$$

and corresponds to the difference between the free energy for the transfer of a polymer segment and a solvent molecule from the bulk to the surface. In the above equations, u_s and u_p are the adsorption energies of a solvent and a segment molecule, respectively, in $k_B T$ units, and φ_s the polymer segment surface fraction representing the chain segments adsorbed on the surface. According to Eq. (27), if a segment is preferentially adsorbed to a solvent molecule, χ_s is positive; moreover, the case of a purely repulsive surface (a wall) is obtained in the limit $\chi_s \rightarrow -\infty$. To calculate φ_s we need to address the issue of how the solid surface affects the statistics of polymer conformations nearby, an issue that is very specific to the details of surface-polymer interactions. In Part II of the present work, the simple case of a neutral wall will be investigated for which φ_s is zero. The more complete case of an adsorbing surface will be separately addressed in a forthcoming paper.

C. Flow-field contributions to the free energy

The third component of the free energy in Eq. (17), h_{def} , is zero under equilibrium (static) conditions. Under nonequilibrium (flow) conditions, h_{def} describes additional changes to the statistics of conformations due to chain deformation from the flow field. These changes are taken into account by evaluating the entropy decrease accompanying the chain deformation and its orientational change. Following Flory,⁵⁰ in order to evaluate this entropy reduction, we need to calculate the configurational entropy change involved in the formation of the deformed state. A key assumption in the original analysis by Flory is that this change can be characterized by a modification in the end-to-end distance by multiplicative scalar factors, α_x , α_y , and α_z along the x , y , and z directions, respectively. In addition, following Flory, it is assumed that the function that describes the distribution of the

polymer end-to-end distance vector is of the same form *before* and *after* deformation; the effect of the deformation is simply to rescale it. For a random chain in the bulk whose end-to-end distance is described by a Gaussian distribution, this approach leads to the following expression (in our notation) for the flow contribution to the free energy:⁵⁰

$$\frac{h_{\text{def}}}{\rho_0 k_B T} = \frac{n_{1,e}}{2} \left(\frac{\alpha_x^2 + \alpha_y^2 + \alpha_z^2 - 3}{2} - \frac{1}{2} \ln(\alpha_x^2 \alpha_y^2 \alpha_z^2) \right). \quad (28)$$

In this form, Flory's theory of polymer elasticity was quite successfully applied to many problems of interest such as the evaluation of the elastic contribution to steric stabilization⁵¹ and the phenomenon of the flow-induced polymer migration in the bulk of viscometric flows.⁵²

However, since an arbitrary flow field simultaneously orients and deforms the polymer molecules in space, such scalars are not adequate to describe the chain deformation and need to be replaced by a tensorial quantity. Moreover, near a confining boundary, the effect of the flow can no longer be captured by a simple rescaling of the equilibrium polymer end-to-end distribution function. Thus, two generalizations are made in this paper: First, it is assumed that the flow imposes a strain on polymer molecules described by a tensor $\boldsymbol{\alpha}$, so that, in order for a particular chain to have an end-to-end vector \mathbf{R} *after* deformation ($\mathbf{R} = \mathbf{r} - \mathbf{r}_0$, where \mathbf{r}_0 and \mathbf{r} are the location vectors for the chain starting and ending points, respectively), it must have had an end-to-end distance vector $\boldsymbol{\alpha}^{-1} \cdot \mathbf{R}$ *before* deformation. Second, it is assumed that the propagator after the flow field has been imposed will, in general, be a new function G' of the coordinate \mathbf{R} (the chain end-to-end vector), the starting location \mathbf{r}_0 and the strain tensor $\boldsymbol{\alpha}$. With this generalization, we can proceed in the analysis in exactly the same way as done by Flory to evaluate the appropriate form for the Boltzmann factor that should enter into the expression for h_{def} . The result is

$$\begin{aligned} \frac{h_{\text{def}}}{\rho_0 k_B T} = & -\frac{1}{2} n_{1,e}(y_0) \int \frac{G(\mathbf{R} + \mathbf{r}_0, N-1; y_0)}{Z(N-1, y_0)} \\ & \times \ln \left[\frac{G'(\mathbf{R} + \mathbf{r}_0, N-1; y_0, \boldsymbol{\alpha})}{Z'(N-1, y_0; \boldsymbol{\alpha})} \right] \\ & \times \frac{Z(N-1, y_0)}{G(\mathbf{R} + \mathbf{r}_0, N-1; y_0)} d^3 \mathbf{R}, \end{aligned} \quad (29)$$

where $\mathbf{r}_0 = (x_0, y_0, z_0)$ denotes the start of the chain, and $Z'(N-1, y_0; \boldsymbol{\alpha})$ is the partition function corresponding to the propagator G' . $G'(\mathbf{r}, n; y_0, \boldsymbol{\alpha})$ denotes the weighted probability that the chain will reach the position \mathbf{r} within $d\mathbf{r}$ in n steps with its start at a distance y_0 above the surface under the applied strain $\boldsymbol{\alpha}$. Of course, in the case of an amorphous bulk chain where the propagator is described by a Gaussian function, and when the tensor $\boldsymbol{\alpha}$ can be diagonalized along the x , y and z directions with α_x , α_y , and α_z in the diagonal, Eq. (29) is easily found to reduce consistently to Eq. (28).

To calculate G' , we make the assumption that, in the deformed state, G' remains Gaussian in the neutral direction z , while in the plane of flow ($x-y$), it obeys a deformed nonisotropic diffusion equation, which we prefer to write in

the space of the eigenvector directions ξ and η of the tensor α . That is, we make the assumption that G' can be decomposed into the product of two distribution functions, one two-dimensional (in general, non-Gaussian) and another one-dimensional Gaussian, $G'_{\xi\eta}$ and G'_z , respectively

$$G'(\mathbf{r}, n; \mathbf{r}_0, \alpha) = G'_{\xi\eta}((\xi, \eta), n; (\xi_0, \eta_0), \alpha) G'_z(z, n; z_0, \alpha), \quad (30)$$

where

$$G'_z = \frac{1}{\sqrt{2\pi c_{zz,n}^0}} \exp\left(-\frac{(z-z_0)^2}{2c_{zz,n}^0}\right). \quad (31)$$

The variance along the z direction, $c_{zz,n}^0$, is exactly the same as in the equilibrium case and coincides with the zz component of the second moment of the distribution function for an n -segment long sub-chain in the bulk. In turn, $G'_{\xi\eta}$ satisfies the following (in general, anisotropic) diffusion equation in the space of the eigenvector directions ξ and η of the tensor α :

$$\frac{\partial G'_{\xi\eta}}{\partial n} = D_1 \frac{\partial^2 G'_{\xi\eta}}{\partial \xi^2} + D_2 \frac{\partial^2 G'_{\xi\eta}}{\partial \eta^2}, \quad (32)$$

where D_1 and D_2 are the two chain “diffusivities” driven by the strain tensor α in the eigenvector directions ξ and η , respectively

$$D_1 = \frac{N-1}{2} b_{\xi\xi}, \quad (33)$$

$$D_2 = \frac{N-1}{2} b_{\eta\eta},$$

with the matrix \mathbf{b} defined through

$$\mathbf{b} = \alpha^2. \quad (34)$$

The scaling of the diffusivities in terms of the apparent strain tensor eigenvalues provides for the distortion of the chain conformations that are anticipated to occur due to the flow.

Equation (32) needs to be solved together with the same initial and boundary conditions as for the equilibrium case, i.e., initial condition the same as in Eq. (21) above and boundary conditions dictated by the physical problem. When Eq. (32) is solved in the bulk with boundary conditions applied at $\pm\infty$, the solution recovered is that of the product of two stretched Gaussians; when such a solution is introduced into Eq. (29), we are led to Eq. (28). Therefore, our scheme extends Flory’s previous analysis on flow induced chain deformations in the bulk to the more general case of chains that are close to a solid boundary.

In summary, by substituting Eqs. (18), (26), and (29) for the various components of the internal part of the free energy h_i into Eq. (17) gives

$$\begin{aligned} \frac{h_i}{\rho_0 k_B T} = & u_s - \varphi_s \chi_s \delta(y) + \frac{1}{2} n_{1,e}(y) \ln \left[\frac{n_{1,e}(y)}{2} \frac{N}{Z(N-1,y)} \right] \\ & + (1 - \varphi(y)) \ln(1 - \varphi(y)) + \chi \varphi(y) (1 - \varphi(y)) \\ & - \frac{1}{2} n_{1,e}(y) \int_0^\infty \frac{G(\mathbf{R} + \mathbf{r}_0, N-1; y)}{Z(N-1,y)} \\ & \times \ln \left[\frac{G'(\mathbf{R} + \mathbf{r}_0, N-1; y, \alpha)}{Z'(N-1, y; \alpha)} \right] \\ & \times \frac{Z(N-1, y)}{G(\mathbf{R} + \mathbf{r}_0, N-1; y)} d^3 \mathbf{R}, \end{aligned} \quad (35)$$

for the internal part of the free energy density, where $n_{1,e}(y)$ and $\varphi(y)$ are not independent quantities but are related to each other through the integral constraint, Eq. (24).

The last step in our analysis is to connect the tensor α with the conformation tensor \mathbf{c} in terms of which the evolution equations have been written. Since α describes the change in the polymer end-to-end distance components over their equilibrium (zero flow) value in a similar fashion as an “apparent strain,” we have

$$\mathbf{c} = \alpha \cdot \mathbf{c}_0 \cdot \alpha^T, \quad (36)$$

which guarantees that the tensor \mathbf{c} itself is symmetric, and where the subscript 0 denotes static equilibrium values, i.e., values calculated by taking into account surface but no flow effects. In the case of interest here, \mathbf{c}_0 has a diagonal form

$$\mathbf{c}_0 = \begin{bmatrix} c_{xx,0} & 0 & 0 \\ 0 & c_{yy,0} & 0 \\ 0 & 0 & c_{zz,0} \end{bmatrix}, \quad (37)$$

where $c_{xx,0} = c_{zz,0} = k_B T / K$ (i.e., they remain at their equilibrium values), whereas $c_{yy,0}$ depends on the distance y from the surface [i.e., $c_{yy,0} = c_{yy,0}(y)$]. This results into the following set of relations (assuming $\alpha_{xz} = \alpha_{yz} = \alpha_{zx} = \alpha_{zy} = \alpha_{zz} = 0$ and $\alpha_{xy} = \alpha_{yx}$):

$$\begin{aligned} c_{xx} &= a_{xx}^2 c_{xx,0} + a_{xy}^2 c_{yy,0}(y), \\ c_{xy} &= a_{xy} (a_{xx} c_{xx,0} + a_{yy} c_{yy,0}(y)), \\ c_{yy} &= a_{xy}^2 c_{xx,0} + a_{yy}^2 c_{yy,0}(y). \end{aligned} \quad (38)$$

In the absence of flow effects, Eq. (35) for the internal free energy density can be directly compared against the one reported by Scheutjens and Fleer.⁵ To within a constant which is proportional to the total number of polymer chains and a function of the number of lattice sites per layer (and, therefore, does not contribute to the minimization procedure), the two expressions are identical provided that the following two correspondences are made: (a) The sum over all possible conformations in the Scheutjens–Fleer lattice model corresponds to an integral over all chain starts in our continuum model, and (b) the ratio ω_c between the number of arrangements of a chain in conformation c and that of a chain in the bulk solution corresponds to the partition function $Z(N-1, y)$, which gives the ratio of the available conformations for a chain starting at y over those for a chain in the bulk.

Using Eq. (35) for the internal part of the free energy density together with the kinetic energy density h_k , one can in principle solve for the polymer density and polymer conformation either by minimizing the total Hamiltonian in case of static equilibrium conditions or by solving the governing equations with suitable boundary conditions in case of flowing conditions. Part II addresses this issue for the case of a dilute polymer solution near a noninteracting surface. An additional issue, however, which should also be resolved before considering this problem is how to calculate the Volterra derivative $\delta H_i / \delta n_1$, i.e., of $\delta H_i / \delta n_{1,e}$ appearing in Eq. (16), in the presence of the integral constraint, Eq. (24). This Volterra derivative plays the role of a generalized chemical potential and appears explicitly in the governing equations. This is addressed in the next section.

IV. THE VOLTERRA DERIVATIVE $\delta H_i / \delta n_{1,e}$

The calculation of $\delta H_i / \delta n_{1,e}$ requires some special handling, because the internal part of the free energy density, h_i , is a function of both $\varphi(y)$ and $n_{1,e}(y)$ which are not independent but are connected through the integral constraint, Eq. (24). Two alternative approaches can be followed: The first one involves the use of a local Lagrange multiplier, and it is the easiest to apply; however, its applicability is strictly limited to static conditions under which the governing equations can be cast into a minimization problem. Thus, a second approach is also presented, which not only does reduce to the same formula as the Lagrange minimization procedure under equilibrium conditions but has also the advantage of being applicable under nonequilibrium conditions. Both of these approaches are presented in Appendix A, and they lead to the following formula for $\delta H_i / \delta n_{1,e}$:

$$\begin{aligned} \frac{1}{k_B T \rho_0} \frac{\delta H_i}{\delta n_{1,e}}(y_0) &= \frac{1}{2} \left[1 + \ln \left(\frac{N}{2} \right) + (\chi - 1)N \right] + \frac{1}{2} \left[\ln n_{1,e}(y_0) \right. \\ &\quad \left. - \sum_{n=0}^{N-1} \int_0^\infty [\ln(1 - \varphi(y)) + 2\chi\varphi(y)] P(y, n; y_0) dy \right] \\ &\quad - \frac{1}{2} \ln Z(N-1, y_0) - \frac{1}{2} \int \frac{G(\mathbf{R} + \mathbf{r}_0, N-1; y_0)}{Z(N-1, y_0)} \\ &\quad \times \ln \left[\frac{G'(\mathbf{R} + \mathbf{r}_0, N-1; y_0, \boldsymbol{\alpha})}{Z'(N-1, y_0; \boldsymbol{\alpha})} \right. \\ &\quad \left. \times \frac{Z(N-1, y_0)}{G(\mathbf{R} + \mathbf{r}_0, N-1; y_0)} \right] d^3 \mathbf{R}, \end{aligned} \quad (39)$$

where $P(y, n; y_0)$ is defined by Eq. (A1.3) of the Appendix. For a dilute polymer solution ($\varphi(y) \ll 1 \forall y$), Eq. (39) reduces to

$$\begin{aligned} \frac{1}{k_B T \rho_0} \frac{\delta H_i}{\delta n_{1,e}}(y_0) &= \frac{1}{2} \left[1 + \ln \left(\frac{N}{2} \right) + (\chi - 1)N \right] + \frac{1}{2} \ln \left(\frac{n_{1,e}(y_0)}{Z(N-1, y_0)} \right) \\ &\quad - \frac{1}{2} \int \frac{G(\mathbf{R} + \mathbf{r}_0, N-1; y_0)}{Z(N-1, y_0)} \\ &\quad \times \ln \left[\frac{G'(\mathbf{R} + \mathbf{r}_0, N-1; y_0, \boldsymbol{\alpha})}{Z'(N-1, y_0; \boldsymbol{\alpha})} \right. \\ &\quad \left. \times \frac{Z(N-1, y_0)}{G(\mathbf{R} + \mathbf{r}_0, N-1; y_0)} \right] d^3 \mathbf{R}. \end{aligned} \quad (40)$$

Thus, the problem boils down to calculating the partition functions $Z(N-1, y_0)$ and $Z'(N-1, y_0; \boldsymbol{\alpha})$, i.e., the propagators $G(\mathbf{R} + \mathbf{r}_0, N-1; y_0)$ and $G'(\mathbf{R} + \mathbf{r}_0, N-1; y_0, \boldsymbol{\alpha})$ in the absence and presence of flow, respectively. For both, the corresponding diffusion equation needs to be solved. In all cases, y is the direction normal to the wall which is assumed to coincide with the coordinate plane $y=0$, x is the flow direction (whenever a flow is applied), and z is the neutral direction.

V. FINAL CONSIDERATIONS

With expression (40) for $\delta H_i / \delta n_{1,e}$, a possible methodology for calculating surface effects on the rheology of a polymer solution can be developed as follows:

(1) Given the type of flow imposed on the solution (for example, extensional or simple shear), the kinematics of the flow and the form of the strain tensor \mathbf{a} are first assumed. For the assumed type of flow, the propagator $G'(\mathbf{R} + \mathbf{r}_0, N-1; y_0, \boldsymbol{\alpha})$ should first be calculated. At this stage, we should keep in mind that calculating $G'(\mathbf{R} + \mathbf{r}_0, N-1; y_0, \boldsymbol{\alpha})$ is not a straightforward task; in general, it is a very formidable problem, since it depends on both the type of flow considered and the solid surface-polymer interactions, the latter dictating the proper boundary conditions. In some cases, however, analytical solutions can be found, as will be seen in Sec. II of the present work for the case of a simple shear flow past a non-interacting surface.

(2) By integrating $G'(\mathbf{R} + \mathbf{r}_0, N-1; y_0, \boldsymbol{\alpha})$ over \mathbf{R} , the partition function $Z'(N-1, y_0; \boldsymbol{\alpha})$ is then calculated as a function of the distance y_0 from the surface and the (as yet unknown) elements of the strain tensor $\boldsymbol{\alpha}$.

(3) Having calculated $G'(\mathbf{R} + \mathbf{r}_0, N-1; y_0, \boldsymbol{\alpha})$ and $Z'(N-1, y_0; \boldsymbol{\alpha})$, the Volterra derivative $\delta H_i / \delta n_{1,e}$ is obtained in terms of y and $\boldsymbol{\alpha}$, by using Eq. (39) or Eq. (40).

(4) This allows us to substitute $\delta H_i / \delta n_{1,e}$ into the macroscopic governing equations and solve for the independent macroscopic variables. The governing equations consist of the concentration equation, Eq. (14), the three components of the momentum equation, Eq. (11), and the equations for the three independent components of the constitutive equation, Eq. (12). These equations can be written either in terms of the conformation tensor \mathbf{c} or in terms of the apparent strain tensor $\boldsymbol{\alpha}$, through Eq. (36) or its equivalent, Eq. (38). Equations (11), (12), (14), (22), (24), (35), and (36) define a closed system of partial differential equations for $\boldsymbol{\alpha}$, $u_x(y)$,

$n_{1,e}(y)$, and $\varphi(y)$, and constitute the final system of equations to be solved. The input data are the number of segments per chain N and the Flory chi-parameter needed in the expression for $\delta H_i / \delta n_{1,e}$, as well as all quantities characterizing the flow field like, for example, the imposed shear stress τ_{yx} , and the bulk fluid (solvent and polymer) viscosities. Results from applying the methodology to the problem of a simple shear flow above a noninteracting solid surface are presented in Part II of this work.

VI. CONCLUSIONS

In this paper, a continuum model has been presented for the study of surface effects on polymer solutions under quiescent and flow conditions, with length resolution down to chain segment size. The model makes use of a generalized free energy formulation and a set of governing equations connecting microscopic parameters to macroscopically observed quantities, derived from the Hamiltonian description of transport phenomena. Within this framework, most of the physics is built into the description of the free energy of the system; this is the most important quantity entering into the governing equations. To define it, a microscopic model for the polymer conformations in the interfacial region needs to be developed. In our work, this is achieved by employing into the analysis not only the polymer segment density but also the polymer chain end density. Thus, polymer conformations are defined by specifying the starting point of every chain and the transition probabilities for its conformations to develop in space.

Within this hierarchical approach, the problem of studying surface effects on the structure and rheology of polymer solutions has been broken down to two different sub-tasks: The first involves calculating the propagator (which describes chain conformations) near the solid surface in the presence of the flow field; the second involves solving the final system of governing equations to get the desired profiles for the given flow field. Through this structured methodology, the new approach permits extending the length scale of analysis near the boundary from the chain size down to the segment length. Thus, it allows, in principle, for a much more systematic modeling of surface- and flow-induced chain deformations than previously possible with continuum approaches, of detail commensurate to the detail of lattice models,⁵ or fully microscopic chain conformation studies,⁶ limited though to static equilibrium only. In the present Part, only the general formulation of the new approach was given. Results from applying it to the problem of a dilute polymer solution flowing near a wall are presented in Part II of the work. Additional results from extending the approach to a polymer solution flowing past an adsorbing surface will be presented in a future work.

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APPENDIX: EVALUATION OF $\delta H_i / \delta n_{1,e}$

1. Through the use of the definition of the Volterra derivative

We want to calculate the Volterra derivative, $\delta H_i / \delta n_{1,e}$, of the functional

$$H_i = \int_0^\infty \left[h_{\text{mix}}(n_{1,e}(y), \varphi(y)) - \frac{k_B T \rho_0}{2} n_{1,e}(y) \right. \\ \times \int \frac{G(\mathbf{R}, N-1; y)}{Z(N-1, y)} \\ \times \ln \left[\frac{G'(\mathbf{R}, N-1; y, \boldsymbol{\alpha})}{Z'(N-1, y; \boldsymbol{\alpha})} \frac{Z(N-1, y)}{G(\mathbf{R}, N-1; y)} \right] d^3 \mathbf{R} \Big] A dy, \quad (\text{A1.1})$$

where the arguments $\varphi(y)$ and $n_{1,e}(y)$ are related by the following equation:

$$\varphi(y) = \frac{1}{2} \sum_{n=0}^{N-1} \int_0^\infty n_{1,e}(y_0) P(y, n; y_0) dy_0, \quad (\text{A1.2})$$

with $P(y, n; y_0)$ defined as

$$P(y, n; y_0) \equiv G(y, n; y_0) \frac{\int_0^\infty G(y', N-1-n; y) dy'}{\int_0^\infty G(y', N-1; y_0) dy'}. \quad (\text{A1.3})$$

The contribution to the Volterra derivative of the second term in Eq. (A1.1) is easily seen to be $-k_B T \rho_0 / 2 \int G(\mathbf{R}, N-1; y) / Z(N-1, y) \ln[G'(\mathbf{R}, N-1; y, \boldsymbol{\alpha}) / Z'(N-1, y; \boldsymbol{\alpha}) Z(N-1, y) / G(\mathbf{R}, N-1; y)] d^3 \mathbf{R}$. What remains is to calculate the contribution of the Flory-Huggins mixing term, H_{mix} , which is a function of both φ and $n_{1,e}$. This consists of two terms: The first is $\partial h_{\text{mix}} / \partial n_{1,e}$ and comes from the direct dependence of h_{mix} on $n_{1,e}$. The second comes from the indirect dependence of h_{mix} on $n_{1,e}$ through its relation with the segment fraction φ by Eq. (A1.2).

To evaluate the second contribution, we make use of the definition of the Volterra derivative of an arbitrary functional F :

$$F(n_{1,e} + \delta n_{1,e}) - F(n_{1,e}) \\ \equiv \int \left[\frac{\delta F}{\delta n_{1,e}(y)} \cdot \delta n_{1,e}(y) \right] A dy \quad \text{as } \delta n_{1,e}(y) \rightarrow 0, \quad (\text{A1.4})$$

where the argument $n_{1,e}$ is meant to be a function, $n_{1,e} = n_{1,e}(y)$, and the limit is to the constant zero function (i.e., the function of a zero value everywhere). Now, we assume that the argument $n_{1,e}(y)$ changes infinitesimally from $n_{1,e}(y)$ to $n_{1,e}(y) + \delta n_{1,e}(y)$. This will result in a change of $\varphi(y)$ from $\varphi(y)$ to $\varphi^*(y)$, given by

$$\varphi^*(y) = \frac{1}{2} \sum_{n=0}^{N-1} \int_0^\infty [n_{1,e}(y_0) + \delta n_{1,e}(y)] P(y, n; y_0) dy_0, \quad (\text{A1.5})$$

which, with the help of Eq. (A1.2), can also be written as

$$\varphi^*(y) - \varphi(y) = \frac{1}{2} \sum_{n=0}^{N-1} \int_0^\infty \delta n_{1,e}(y_0) P(y, n; y_0) dy_0. \quad (\text{A1.6})$$

Since H_{mix} is a function of both $n_{1,e}(y)$ and $\varphi(y)$, the change in H_{mix} upon changing $n_{1,e}(y)$ from $n_{1,e}(y)$ to $n_{1,e}(y) + \delta n_{1,e}(y)$ can be expressed as follows:

$$\begin{aligned} H_{\text{mix}}(n_{1,e} + \delta n_{1,e}) - H_{\text{mix}}(n_{1,e}) \\ = \int_0^\infty \left[\frac{\partial h_{\text{mix}}}{\partial n_{1,e}} \delta n_{1,e} + \frac{\partial h_{\text{mix}}}{\partial \varphi}(y) \cdot [\varphi^*(y) - \varphi(y)] \right] A dy, \end{aligned} \quad (\text{A1.7})$$

i.e.,

$$\begin{aligned} H_{\text{mix}}(n_{1,e} + \delta n_{1,e}) - H_{\text{mix}}(n_{1,e}) \\ = \int_0^\infty \left[\frac{\partial h_{\text{mix}}}{\partial n_{1,e}} \delta n_{1,e} + \frac{1}{2} \frac{\partial h_{\text{mix}}}{\partial \varphi}(y) \right. \\ \left. \times \left(\int_0^\infty \delta n_{1,e}(y_0) \sum_{n=0}^{N-1} P(y, n; y_0) dy_0 \right) \right] A dy, \end{aligned} \quad (\text{A1.8})$$

or, equivalently

$$\begin{aligned} H_{\text{mix}}(n_{1,e} + \delta n_{1,e}) - H_{\text{mix}}(n_{1,e}) \\ = \int_0^\infty \frac{\partial h_{\text{mix}}}{\partial n_{1,e}} \delta n_{1,e} A dy + \frac{1}{2} \int_0^\infty \int_0^\infty \frac{\partial h_{\text{mix}}}{\partial \varphi}(y) \\ \times \sum_{n=0}^{N-1} P(y, n; y_0) \delta n_{1,e}(y_0) dy A dy_0. \end{aligned} \quad (\text{A1.9})$$

In the last equation, y and y_0 are dummy indices; therefore, they can be interchanged, which, after collecting common factors together, helps casting Eq. (A1.9) into the following form:

$$\begin{aligned} H_{\text{mix}}(n_{1,e} + \delta n_{1,e}) - H_{\text{mix}}(n_{1,e}) \\ = \int_0^\infty \frac{\partial h_{\text{mix}}}{\partial n_{1,e}} \delta n_{1,e}(y) A dy + \int_0^\infty \delta n_{1,e}(y) \left(\frac{1}{2} \int_0^\infty \right. \\ \left. \times \frac{\partial h_{\text{mix}}}{\partial \varphi} \times (y_0) \sum_{n=0}^{N-1} P(y_0, n; y) dy_0 \right) A dy. \end{aligned} \quad (\text{A1.10})$$

Comparison of the last equation against Eq. (A1.4), the definition equation of the Volterra derivative, suggests that

$$\frac{\delta H_{\text{mix}}}{\delta n_{1,e}} = \frac{\partial h_{\text{mix}}}{\partial n_{1,e}} + \frac{1}{2} \int_0^\infty \frac{\partial h_{\text{mix}}}{\partial \varphi}(y_0) \sum_{n=0}^{N-1} P(y_0, n; y) dy_0. \quad (\text{A1.11})$$

This is the desired result. By collecting then all contributions to the Volterra derivative $\delta H_i / \delta n_{1,e}$ we get that

$$\begin{aligned} \frac{\delta H_i}{\delta n_{1,e}} = - \frac{k_B T \rho_0}{2} \int \frac{G(\mathbf{R}, N-1; y)}{Z(N-1, y)} \\ \times \ln \left[\frac{G'(\mathbf{R}, N-1; y, \boldsymbol{\alpha})}{Z'(N-1, y; \boldsymbol{\alpha})} \frac{Z(N-1, y)}{G(\mathbf{R}, N-1; y)} \right] d^3 \mathbf{R} \\ + \frac{\partial h_{\text{mix}}}{\partial n_{1,e}} + \frac{1}{2} \int_0^\infty \frac{\partial h_{\text{mix}}}{\partial \varphi}(y_0) \\ \times \sum_{n=0}^{N-1} P(y_0, n; y) dy_0, \end{aligned} \quad (\text{A1.12})$$

which is the relation that we wanted to obtain.

2. Through the use of a local Lagrange multiplier

This approach is valid only for static equilibrium conditions. In this case, the defining equation is of the form

$$\frac{\delta(H_i - H_{i,b})}{\delta n_{1,e}} = 0, \quad (\text{A2.1})$$

where H_i and $H_{i,b}$ (the internal part of the free energy in the bulk) are functions of φ and $n_{1,e}$ which are constrained through Eq. (A1.2). In order to take the constraint into account, we make use of a local Lagrange multiplier, $\varphi(y)$, and we form a new functional

$$\begin{aligned} F(n_{1,e}, \varphi, \lambda) = \int_0^\infty h_i(\varphi(y), n_{1,e}(y)) dy + \int_0^\infty \lambda(y) \left(\varphi(y) \right. \\ \left. - \frac{1}{2} \int_0^\infty n_{1,e}(y_0) \sum_{n=0}^{N-1} P(y, n; y_0) dy_0 \right) A dy, \end{aligned} \quad (\text{A2.2})$$

where h_i denotes the internal free energy (in fact, it is the internal free energy minus the corresponding expression in the bulk). As was shown above, the last term on the right-hand side gives rise to a double integration, whose two dummy indices, y and y_0 , can be interchanged so that the functional F takes the form

$$\begin{aligned} F(n_{1,e}, \varphi, \lambda) = \int_0^\infty \left(h_i(\varphi(y), n_{1,e}(y)) + \lambda(y) \varphi(y) \right. \\ \left. - \frac{1}{2} n_{1,e}(y) \int_0^\infty \lambda(y_0) \sum_{n=0}^{N-1} P(y_0, n; y) dy_0 \right) A dy. \end{aligned} \quad (\text{A2.3})$$

The equilibrium conditions then become

$$\begin{aligned} \frac{\partial F}{\partial \varphi} = 0, \\ \frac{\partial F}{\partial n_{1,e}} = 0, \\ \frac{\partial F}{\partial \lambda} = 0, \end{aligned} \quad (\text{A2.4})$$

from which we get

$$\frac{\partial h_i}{\partial \varphi}(y) + \lambda(y) = 0,$$

$$\frac{\partial h_i}{\partial n_{1,e}}(y) - \frac{1}{2} \int_0^\infty \lambda(y_0) \sum_{n=0}^{N-1} P(y_0, n; y) dy_0 = 0, \quad (\text{A2.5})$$

$$\varphi(y) - \frac{1}{2} \int_0^\infty n_{1,e}(y_0) \sum_{n=0}^{N-1} P(y, n; y_0) dy_0 = 0.$$

Elimination of the parameter $\lambda(y)$ in the last three equations and substitution of h_i then leads to the following conditions:

$$\begin{aligned} & -\frac{k_B T \rho_0}{2} \int \frac{G(\mathbf{R}, N-1; y)}{Z(N-1, y)} \\ & \times \ln \left[\frac{G'(\mathbf{R}, N-1; y, \mathbf{a})}{Z'(N-1, y; \mathbf{a})} \frac{Z(N-1, y)}{G(\mathbf{R}, N-1; y)} \right] d^3 \mathbf{R} \\ & + \frac{\partial h_{\text{mix}}}{\partial n_{1,e}}(y) + \frac{1}{2} \int_0^\infty \frac{\partial h_{\text{mix}}}{\partial \varphi}(y_0) \sum_{n=0}^{N-1} P(y_0, n; y) dy_0 = 0, \\ & \varphi(y) - \int_0^\infty \frac{1}{2} n_{1,e}(y_0) \sum_{n=0}^{N-1} P(y, n; y_0) dy_0 = 0, \end{aligned} \quad (\text{A2.6})$$

which are in complete agreement with the conditions obtained through the definition of the Volterra derivative when $\delta H_i / \delta n_{1,e} = 0$.

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