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Molecular Thermodynamics of Polymer Melts at Interfaces

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by

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ABSTRACT

A lattice model is developed for the prediction of structure and thermodynamic properties at free polymer melt surfaces and polymer melt/solid interfaces. Density variations in the interfacial region are taken into account by introducing voids in the lattice, in the spirit of the equation of state theory of Sanchez and Lacombe. Intramolecular energy (chain stiffness) effects are explicitly incorporated. The model is derived through a rigorous statistical mechanical and thermodynamic analysis, which is based on the concept of availability. Two cases are considered: "full equilibrium", whereby the interfacial polymer is taken as free to exchange heat, work and mass with a bulk polymer phase at given temperature and pressure; and "restricted equilibrium", whereby a thin polymer film is allowed to equilibrate locally in response to ambient temperature and pressure, but in which chains do not necessarily have the same chemical potential as in the unconstrained bulk. Our free equilibrium formulation in a melt of freely jointed chains is mathematically similar to the solution model of Scheutjens and Fleer. Techniques are developed for calculating surface tension, adhesion tension, density profiles, chain shape, bond orientation, as well as the distribution of segments of various orders in the interfacial region. The expression derived for surface tension is fully consistent with the "mechanical" definition of this property. In the continuum limit, our lattice model reduces to an integrodifferential system, very reminiscent of previous self-consistent field approaches.

I. INTRODUCTION

The surface and interfacial behavior of polymers in the condensed, solventless state is relevant to many technical applications. The free surface properties of amorphous polymers are of interest in the manufacture of materials exhibiting controlled wetting characteristics, or biocompatibility. Polymer melt/solid interfaces are important in adhesion, lubrication and polymer processing. Glassy polymer/solid interfaces govern the mechanical response of composite materials, as well as the performance of resists, encapsulants and dielectrics. To judiciously select and efficiently design materials for these and similar applications, we need to understand the relationships between polymer chemical structure and macroscopically manifested interfacial properties at the molecular level. Adsorptive segment-solid interactions, or the lack thereof in polymer/gas systems, as well as entropic constraints imposed by a polymer surface, cause the conformation of polymer chains to deviate from what it is in the unconstrained bulk. Perturbations in local structure lead, in turn, to unique, spatially dependent thermodynamic, transport, mechanical and optical properties in the interfacial region.

The adsorption of polymers from solution on solid surfaces has been studied in considerable detail, in connection with the steric stabilization of colloids. A concrete and particularly successful lattice model for this situation was developed by Scheutjens and

Fleer¹. Much less attention has been devoted to the behavior of bulk polymers at interfaces, however. Previous theoretical approaches on this subject can be roughly divided into two categories: efforts to elucidate surface structure, and efforts to predict surface tension. Weber and Helfand² briefly considered the structure of an infinite-molecular weight polymer melt near an impenetrable, nonadsorbing plane barrier in the context of a lattice treatment of polymer solutions. An ingeniously simple lattice model was developed by Dill and Flory for describing bond orientation effects in lipid bilayer membranes³. More recently, a Monte Carlo simulation of the free surface structure of a polymer melt was performed by Madden, using an interesting pseudokinetic algorithm to sample configuration space⁴. As regards the prediction of surface tension, we mention here a successful phenomenological treatment by Sanchez and Poser⁵, which combines the Cahn-Hilliard theory of nonuniform systems with a lattice-based equation of state, developed by Sanchez and Lacombe⁶. Despite these efforts, there exists today no unified theoretical approach, that can both provide realistic estimates of polymer surface tension and a detailed, consistent picture of interfacial structure. Moreover, the solid/polymer interface problem is largely unexplored. A theory is needed, that can explicitly incorporate segment/surface interactions and their effects on interfacial structure and properties.

The objective of this work has been to develop a simple statistical mechanical model, involving no adjustable parameters, that (a) is capable of predicting the chain-length and temperature

dependence of surface tension of macromolecular liquids; (b) provides a detailed picture of structure at free polymer surfaces and polymer/solid interfaces, and of its dependence on chain constitution, molecular weight, segment-solid interactions, and temperature; (c) can be used to explore the thermodynamics and structure of polymer melts confined between closely spaced solid surfaces. A lattice modeling approach is used. Despite their limitations⁷, lattice models can preserve the basic physics, and at the same time are simple enough to permit a tractable analytical formulation of the problems at hand. A constant density lattice approach for homopolymers at interfaces has been presented in a previous publication⁸. Here we introduce a more refined model, that incorporates density variations in the interfacial region, and is based on rigorous thermodynamic analysis.

The purpose of this paper is to present the fundamental theory of the variable density lattice model. In section II the model assumptions are introduced, and a statistical mechanical analysis is performed to obtain expressions for the relevant free energy quantity (the availability) in the interfacial region and in the bulk, in terms of molecular information. In section III a thermodynamic formulation is presented, that assumes full equilibrium between interfacial and unconstrained bulk polymer. Using the statistical mechanical expressions derived in section II, a closed set of algebraic equations is developed, that we will term the "full equilibrium model". Section IV is concerned with an alternative thermodynamic formulation, which assumes that the interfacial polymer

equilibrates partially independently of the bulk, "feeling" the bulk only through its temperature and pressure. The resulting model we will call the "restricted equilibrium model". Techniques for obtaining structural features from either the full equilibrium or the restricted equilibrium model solution are summarized in Section V. Section VI is concerned with some interesting mathematical aspects of the variable density lattice model, and with its connections to a continuum formulation, that has been used in the past for polymers at interfaces.

II. STATISTICAL MECHANICAL ANALYSIS

The system examined in this work is depicted in Fig.1. We consider a monodisperse homopolymer melt, lying between two flat surfaces, in contact with unconstrained bulk polymer. Three phases are distinguished: The solid (non-polymer) phase s , the interfacial polymer phase f , and the bulk polymer b . For studying free polymer surfaces, the solid phase is substituted by an energetically neutral gas phase. Note that, in the latter case, the planar polymer film f is inherently metastable; in the absence of external fields it would break and incorporate itself into the bulk polymer surrounding it, to minimize surface area. Our approach rests on the following assumptions:

1. The solid plates are molecularly smooth and energetically homogeneous. Their extent in the x - and y - directions is taken as

effectively infinite, and end effects are neglected. Also, the solid phase is impenetrable by the polymer and completely incompressible. The structure and density of the solid are not affected by the presence of adsorbed polymer in any way.

2. The polymer is composed of identical, linear chains. In both phases f and b the polymer is represented as a simple cubic lattice, whose sites are filled by chain segments (beads) and voids. The bulk polymer phase is taken as infinite in extent. The density of the polymer phase is variable; it can adjust to changes in temperature, pressure, as well as to the special energetic and entropic conditions prevailing at the interface, through changes in the local concentration of voids.
3. In laying down chains in the model polymer lattice, the Bragg-Williams approximation of random mixing will be used, to account for excluded volume effects in a layerwise fashion¹. The probability of a segment being added to a given lattice layer will be taken proportional to the fraction of sites not yet occupied in that layer. Configurational entropy will be obtained using the simple "Flory"⁹ (or large coordination limit) approximation, as opposed to a more elaborate, Guggenheim-type treatment^{6,10}. A layerwise mean field approximation is also used in calculating the potential energy of segment-segment interactions, as well as in estimating intramolecular energy.

According to assumption 2 polymer chains are all of the type A_r , where A symbolizes a segment and r is the chain length. The repulsive

potential between segments at very small separations is taken into account by forbidding multiple occupancy of lattice sites by segments, as shown below. Attractive (e.g. London dispersion) interactions are represented by a characteristic energy, w_{AA} , which is active between each pair of chain segments that occupy adjacent lattice sites, regardless of whether they belong to the same or to different chains. Segments directly connected by a bond contribute a constant potential energy w_{AA} per pair. The volume of a segment, $v^*/N_L = (\ell^*)^3$, defines the lattice size for a given polymer. Adsorptive interactions will be considered as active only between segments adjacent to a solid surface and sites on that surface. A characteristic potential energy w_{AS} will be contributed by each adsorbed segment.

In addition, the conformational energy (intramolecular stiffness) of chains will be considered in some calculations. To account for this in an elementary way, we distinguish between three "conformational states" in our lattice chains, which we designate as "trans", "gauche" and "backstepping", as shown in Fig.2. This assignment of states is made in the spirit of Di Marzio and Rubin's work¹¹. The conformational state around segment s ($1 \leq s \leq r$) is set by the relative placement of the pair of bonds $(s-1, s)$, that flank this segment. A characteristic energy is thus associated with each of the $(r-2)$ "triplets" of segments along a chain. Trans is chosen as the reference for intramolecular energy, whereas gauche and backstepping are characterized by energies ϵ_L and ϵ_V relative to trans. Note that this simple lattice definition

is to be distinguished from that used with realistic chain models¹²; in the latter, a conformational state is set by the torsion angle of a skeletal bond (rather than by the intramolecular environment around a segment), and affects the relative disposition of three (rather than two) bonds. The "backstepping" conformational state is used as an additional measure for preventing multiple occupancy of sites.

A representation of bulk polymers as lattices filled with chains and voids has been used by Sanchez and Lacombe⁶. Apart from the consideration of intramolecular energy, the molecular picture invoked here is completely consistent with theirs. Sanchez and Lacombe's work led to a successful equation of state for macromolecular fluids, in which the nature of the fluid is expressed through three parameters: r , w_{AA} and v^* ; or, equivalently, r , T^* and P^* , where

$$\left. \begin{aligned} T^* &= -z \frac{w_{AA}}{2k} \\ P^* &= \frac{RT^*}{v^*} \end{aligned} \right\} \quad (1)$$

The parameter T^* is a temperature characteristic of segment-segment interactions. The parameter P^* is a characteristic pressure, indicative of the cohesive energy density of the fluid. By fitting values of r , T^* , and P^* to experimental data, Sanchez and Lacombe were able to reproduce the phase and volumetric behavior of low-molecular weight liquids and high polymers quite accurately. Polymer melt densities were fitted by Sanchez and Lacombe with a relative error of less than 1%, within rather wide ranges of pressure and

temperature⁶. Moreover, by checking experimental solubility parameters¹³ against the Sanchez-Lacombe estimate:

$$\delta^2 = P^* \phi_b^2 \quad (2)$$

(where ϕ_b the volume fraction of segments in the lattice) one can confirm that the Sanchez-Lacombe model is quite satisfactory in describing cohesive forces in the bulk.

We will be using the Sanchez-Lacombe parameters in all calculations reported here. For the sake of symmetry with Eq.(1) we will also introduce the characteristic temperatures T_s^* , T_L and T_V , in lieu of the energies w_{AS} , ϵ_L and ϵ_V , respectively:

$$\left. \begin{aligned} T_s^* &= - \frac{w_{AS}}{k} \\ T_L &= \frac{\epsilon_L}{k} \\ T_V &= \frac{\epsilon_V}{k} \end{aligned} \right\} \quad (3)$$

In the most general case the molecular characteristics of the system are summarized in the six parameters r , T^* , P^* , T_s^* , T_L and T_V . In the free interface problem T_s^* is identically equal to zero.

Developing a model for the interfacial system under investigation amounts to deriving an appropriate expression for "free energy" in terms of thermodynamic variables and molecular characteristics, and subsequently minimizing this free energy function, to impose the conditions of equilibrium. The three phases present will be assumed thermally equilibrated at all times:

$$T_s = T_f = T_b = T \quad (4)$$

Since density can vary in the polymer phase, pressure appears as a variable. Let P_b be the pressure in the bulk polymer phase. Pressure is not constant throughout the system of Fig.1. In fact, pressure in the interfacial region is anisotropic, and the integral of the difference between bulk and transverse pressure is directly related to interfacial tension^{14,15,16}. The question thus arises, what pressure should one use in defining a "free energy" for the system. The answer is provided in Modell and Reid's superb textbook of thermodynamics¹⁷. By consideration of a system containing interfaces, at equilibrium with a constant temperature and a constant pressure reservoir, it is rigorously shown there that the appropriate "free energy" quantity is the availability, a generalized Gibbs energy, defined in each phase using the temperature and pressure of the reservoirs. In our system, the infinite (Assumption 2) bulk polymer phase plays the role of a constant temperature and pressure reservoir, at T and P_b .

Availability $\bar{r}$ is defined in each phase from the internal energy, volume and entropy of that phase by¹⁸:

$$\bar{r}_\alpha = \bar{U}_\alpha + P_b \bar{V}_\alpha - T \bar{S}_\alpha \quad (\alpha=s,f,b) \quad (5)$$

Only in the bulk polymer phase is availability coincident with Gibbs energy. At equilibrium the total availability of the system is at a minimum. In the following, use of the ill-defined term "free energy" will be systematically avoided, and the precise terms Gibbs energy, Helmholtz energy and availability will be used instead.

Our objective in this section is to develop expressions for the availability of the interfacial polymer (γ_f) and of the bulk polymer (γ_b) by a statistical mechanical analysis of the lattice model. Using these expressions, we will impose the condition of thermodynamic equilibrium, and thereby provide closure to the model, in sections III and IV.

A. Availability of the Interfacial Polymer

Consider a part of the model system depicted in Fig.1, that consists of two equal, parallel and opposite sections of the s-surfaces, together with the f-polymer in between. The surface sections are of macroscopic dimensions in the x- and y- directions; they may be chosen so as to coincide with the entire s- surfaces. Let n_f be the number of chains between the considered surface sections,

$$h = 2m\ell^* \quad (6)$$

be their separation, $\underline{a}$ the area of each section and

$$L = N_L \underline{a} / a^* = \underline{a} / (\ell^*)^2 \quad (7)$$

the total number of sites on each surface section.

By assumption 2 the interfacial polymer is represented as a cubic lattice of $2m$ layers, between the solid surfaces. We will use the index i ($1 \leq i \leq 2m$) for numbering successive lattice layers. Average structural and thermodynamic properties will be symmetric with respect to the midplane between layers m and $m+1$. We will also use the index s ($1 \leq s \leq r$) to count segments along the backbone of a chain. Following the treatment of Scheutjens and Fleer^{1,8} we will define a conformation as the ordered r -ad of layer numbers, on which successive segments find themselves:

$$\{ k(s,c) \} \quad 1 \leq s \leq r \quad (8)$$

Let $\lambda_0 = 2/3$ be the fraction of nearest neighbor sites to a given site that belong to the same layer as the considered site, $\lambda_1 = \frac{1}{2} (1 - \lambda_0)$, and $z=6$ the coordination number of the lattice. With the Scheutjens and Fleer definition, there is a number of different arrangements that correspond to the same conformation. This number is given by:

$$L z^{r-1} \prod_{s=1}^{r-1} (\lambda_{s,s+1})_c = L z^{r-1} \omega_c \quad (9)$$

where we used the notation:

$$(\lambda_{s,s+1})_c = \begin{cases} \lambda_0, & \text{if } k(s,c) = k(s+1,c) \\ \lambda_1, & \text{if } |k(s,c) - k(s+1,c)| = 1 \end{cases} \quad (10)$$

The sequence $(\lambda_{s,s+1})_c$ ($1 \leq s \leq r-1$) and, therefore, the factor ω_c , are uniquely defined, given a conformation c . Backfolding of chains is not excluded, a priori, in this definition of conformations. [Note the use of z , rather than $(z-1)$, for all segments in Eq.(9).]

Our objective is to analyze the system of n_f interfacial polymer chains at constant temperature T , bulk polymer pressure P_b , and plate separation h . In the model representation used here, microscopic states of this system are to be specified in configuration space by (a) the number of sites on each surface, L ; (b) the number of chains, n_c , that belong to each conformation; and (c) the numbers of voids, n_i^o , in each lattice layer. Let us designate a given set of values $[L, \{n_c\}, \{n_i^o\}]$ as a "microstate". The quantities L , n_c and n_i^o are not independent. They obey the constraints:

$$L = \sum_c n_c r_{i,c} + n_i^o \quad 1 \leq i \leq 2m \quad (11)$$

and

$$n_f = \sum_c n_c \quad (12)$$

where

$$r_{i,c} = \sum_{s=1}^r \delta_{i,k(s,c)} \quad (13)$$

is the number of lattice sites occupied in layer i by conformation c . Eq.(11) expresses the impossibility of multiple occupancy of sites by chain segments in layer i . Note that multiple occupancy is not excluded on a site-by-site basis, but on a "smeared", layer-by-layer basis, to preserve the one-dimensional character of the model. There may be, in principle, some doubly occupied sites in layer i , but each will cost an additional void in that layer. Eq.(12) is simply a population balance of chains.

The total potential energy of the system in the microstate $\{ L, \{n_c\}, \{n_i^o\} \}$ comes from three contributions: (a) attractive segment-segment interactions; (b) adsorptive segment-surface interactions; (c) intrachain (conformational) energy:

$$\begin{aligned} E_f \left[L, \{n_c\}, \{n_i^o\} \right] &= E_f \left[L, \{n_c\} \right] = \\ &= E_{f,AA} \left[L, \{n_c\} \right] + E_{f,AS} \left[L, \{n_c\} \right] + E_{f,intra} \left[L, \{n_c\} \right] \end{aligned} \quad (14)$$

To determine $E_{f,AA}$ we consider a segment in layer i . This segment has

$z \lambda_{j-i}$ nearest neighbor sites in layer j , where:

$$\lambda_{j-i} = \begin{cases} \lambda_{|j-i|} & \text{for } |j-i| \leq 1 \\ 0 & \text{for } |j-i| > 1 \end{cases} \quad (15)$$

Of these $z \lambda_{j-i}$ nearest neighbor sites some will be occupied by chain segments, and some will be void. The expected fraction occupied is

$$\text{equal to } \frac{1}{L} \sum_c n_c r_{j,c}.$$

$$\sum_c n_c r_{j,c}$$

The quantity $z \lambda_{j-i} \frac{\sum_c n_c r_{j,c}}{L} w_{AA}$ is the expected attractive

energy contributed by interactions between the considered segment and segments in layer j ; and the quantity

$$\sum_{j=1}^{2m} z \lambda_{j-i} \frac{\sum_c n_c r_{j,c}}{L} w_{AA} \text{ is the total expected energy due to}$$

interactions in which the considered segment in layer i participates.

There are $\sum_c n_c r_{i,c}$ segments in layer i . By summing all interaction

energies from pairs in which these segments participate, and

subsequently summing over all lattice layers, we reach the result:

$$E_{f,AA}(L, \{n_c\}) = \frac{1}{2} \sum_{i=1}^{2m} \left\{ \sum_c n_c r_{i,c} \left[\sum_{j=1}^{2m} z \lambda_{j-i} \frac{\sum_c n_c r_{j,c}}{L} \right] \right\} w_{AA} \quad (16)$$

The factor $1/2$ in Eq.(16) corrects for counting the interactions

twice, once for each segment participating in a pair. Again, Eq.(16)

is not exact; in counting interactions it invokes a mean field approximation, to preserve model simplicity (Assumption 3).

For the segment-surface part of the potential in the considered microstate we can write:

$$E_{f,AS} \left(L, \{n_c\} \right) = z \lambda_1 \left\{ \sum_c n_c \left[r_{1,c} + r_{2m,c} \right] \right\} w_{AS} \quad (17)$$

The intramolecular energy contribution becomes:

$$E_{intra} \left(L, \{n_c\} \right) = \sum_c n_c \left\{ \sum_{s=1}^{r-2} \epsilon \left[k(s+1,c) - k(s,c), k(s+2,c) - k(s+1,c) \right] \right\} = \sum_c n_c \epsilon_c \quad (18)$$

Here, $\epsilon \left[k(s+1,c) - k(s,c), k(s+2,c) - k(s+1,c) \right]$ is the conformational energy contribution due to the relative placement of bonds s and $(s+1)$ in conformation c , to be expressed in terms of the quantities ϵ_L and ϵ_V , introduced above; ϵ_c is the total intramolecular energy of chain conformation c . Note that, in assigning a unique value to the conformational energy around segment s in conformation c , we have implicitly invoked a mean field approximation: With our definition of conformations the angle between bonds s and $(s+1)$ is not uniquely specified if segments s , $(s+1)$ and $(s+2)$ all lie in the same layer.

Combining Eqs. (14) to (18) we obtain:

$$E_f \left(L, \{n_c\}, \{n_i^o\} \right) = \frac{1}{2} \sum_{i=1}^{2m} \left\{ \sum_c n_c r_{i,c} \left[\sum_{j=1}^{2m} z \lambda_{j-i} \frac{\sum_c n_c r_{j,c}}{L} \right] \right\} w_{AA^+} \quad (19)$$

$$+ z \lambda_1 \left\{ \sum_c n_c \left[r_{1,c} + r_{2m,c} \right] \right\} w_{AS} + \sum_c n_c \epsilon_c$$

The microstate $\{ L, \{n_c\}, \{n_i^o\} \}$ is degenerate. It can be realized through many configurations of the multichain interfacial system. The number of ways $\Omega[L, \{n_c\}, \{n_i^o\}]$, in which the set of conformations $\{n_c\}$ and voids $\{n_i^o\}$ can be arranged in the lattice, is calculated as in the solution work of Scheutjens and Fleer^{1,8}. The result, based on the Bragg-Williams approximation of random mixing, is:

$$\Omega_f[L, \{n_c\}, \{n_i^o\}] = (L!)^{2m} \left[\frac{z}{L} \right]^f \prod_c \frac{\omega_c^{n_c}}{n_c!} \left[\prod_{i=1}^{2m} \frac{1}{n_i^o!} \right] \quad (20)$$

Using the formalism of the isothermal-isobaric ensemble (constant n_f, T, P_b, h) we can now write the availability of the interfacial polymer as:

$$\begin{aligned} \underline{T}_f(T, P_b, n_f, h) = -kT \ln & \left\{ \sum_{\substack{L=0 \\ \text{compatible} \\ \text{with constraints} \\ \text{between phase f} \\ \text{and its environment}}}^{\infty} \sum_{\substack{\{n_c\}, \{n_i^o\} \\ \text{compatible} \\ \text{with constraints in} \\ \text{Eqs. (11), (12)}}} \Omega_f[L, \{n_c\}, \{n_i^o\}] \right. \\ & \left. \exp \left[- \frac{1}{kT} \left[E_f[L, \{n_c\}, \{n_i^o\}] + P_b \frac{v^*}{N_L} (2mL) \right] \right] \right\} \quad (21) \end{aligned}$$

To proceed further, we introduce a maximum term approximation^{6,19}. The summand appearing in the isothermal-isobaric partition function [double sum in Eq.(21)] is expected to be strongly peaked at a certain set of values of the microscopic degrees of freedom $L, \{n_c\}, \{n_i^o\}$. We will substitute the entire partition function by this

maximum value of the summand. In the following we will be using the symbols L , $\{n_c\}$, $\{n_i^o\}$ to denote the values of the degrees of freedom at this optimal point. The optimization with respect to L at constant T , h , P_b and n_f will be performed in the context of the thermodynamic analysis of Sections III and IV. What is meant by "constraints between phase f and its environment" will be elucidated there. The optimization with respect to the conformation and void distributions $\{n_c\}$ and $\{n_i^o\}$ will be performed here. By virtue of the maximum term approximation, we rewrite Eq.(21) as:

$$\underline{\gamma}_f(T, P_b, n_f, \underline{a}, h) = -kT \ln \Omega_f(L, \{n_c\}, \{n_i^o\}) + E_f(L, \{n_c\}, \{n_i^o\}) + P_b \frac{v}{N_L} (2mL) \quad (22)$$

The surface area, $\underline{a}$, has been inserted among the arguments of $\underline{\gamma}_f$ as a reminder of the fact that the optimization with respect to L has not yet been performed. At equilibrium, only four of the thermodynamic variables T , P_b , n_f , $\underline{a}$ and h are independent.

We now determine the conformation and void distribution that maximizes the summand in equation (21) for given values of T , P_b , n_f , m and L , under the constraints (11) and (12). Omitting the constant pressure-volume term we can state the maximization problem as follows:

$$\begin{array}{l} \text{Maximize} \\ \text{the function:} \end{array} \quad \ln \Omega_f(L, \{n_c\}, \{n_i^o\}) - \frac{1}{kT} E_f(L, \{n_c\}, \{n_i^o\}) \quad (23)$$

with respect to n_c (all c compatible with given m and L)
and n_i^o $1 \leq i \leq 2m$

under the segment balance constraints in individual lattice layers:

$$\sum_c n_c r_{i,c} + n_i^o = L \quad 1 \leq i \leq 2m \quad (11)$$

and the chain balance constraint:

$$n_f = \sum_c n_c \quad (12)$$

Physically, this constrained optimization imposes the condition of internal equilibrium within the interfacial polymer; i.e., it requires that chains have the same chemical potential throughout the interfacial region⁸. Introducing a Lagrange multiplier ζ_i for each of the constraints (11), and a Lagrange multiplier ξ for the constraint (12), we require that the following augmented objective function have a stationary point with respect to $\{n_c\}$, $\{n_i^o\}$, $\{\zeta_i\}$ and ξ at the sought optimal point:

$$\begin{aligned} F_f(\{n_c\}, \{n_i^o\}, \{\zeta_i\}, \xi) = & \ln \left[\Omega_f(L, \{n_c\}, \{n_i^o\}) \right] - \frac{1}{kT} E_f(L, \{n_c\}, \{n_i^o\}) - \\ & - \sum_{i=1}^{2m} \zeta_i \left[\sum_c n_c r_{i,c} + n_i^o - L \right] - \xi \left[\sum_c n_c - n_f \right] \end{aligned} \quad (24)$$

Using Eqs.(19) and (20) in Eq.(24), and invoking Stirling's approximation for all factorials, we obtain:

$$\begin{aligned}
F_f \left(\{n_c\}, \{n_i^0\}, \{\zeta_i\}, \xi \right) = & 2mL \ln L - 2mL + (r-1) n_f \ln z - (r-1) n_f \ln L + \\
& + \sum_c n_c \ln \omega_c - \sum_c n_c \ln n_c + \sum_c n_c - \sum_{i=1}^{2m} n_i^0 \ln n_i^0 + \sum_{i=1}^{2m} n_i^0 - \\
& - \left(\frac{z w_{AA}}{2kT} \right) \sum_{i=1}^{2m} \left\{ \sum_c n_c r_{i,c} \left[\sum_{j=1}^{2m} \left(\lambda_{j-i} \frac{\sum_c n_c r_{j,c}}{L} \right) \right] \right\} - \\
& - \left(\frac{\lambda_1 z}{kT} w_{AS} \right) \left\{ \sum_c n_c (r_{1,c} + r_{2m,c}) \right\} - \sum_c n_c \left(\frac{\epsilon_c}{kT} \right) - \\
& - \sum_{i=1}^{2m} \zeta_i \left(\sum_c n_c r_{i,c} + n_i^0 - L \right) - \xi \left(\sum_c n_c - n_f \right)
\end{aligned} \tag{25}$$

To simplify notation we introduce, following references 1 and 8, the interaction parameters:

$$\left. \begin{aligned}
x &= - \frac{z w_{AA}}{2kT} = \frac{T^*}{T} \\
x_s &= - \frac{\lambda_1 z}{kT} \left(w_{AS} - \frac{1}{2} w_{AA} \right) = \lambda_1 \left(\frac{z T_s^* - T^*}{T} \right)
\end{aligned} \right\} \tag{26}$$

A stationary point of F_f implies the following set of conditions:

$$\begin{aligned}
\left. \frac{\partial F_f}{\partial n_c} \right|_{n_c, \neq c, n_i^0, \zeta_i, \xi} = & - \ln \left(\frac{n_c}{\omega_c} \right) - \frac{\epsilon_c}{kT} + \frac{2x}{L} \sum_{i=1}^{2m} r_{i,c} \left[\sum_{j=1}^{2m} \lambda_{j-i} \left(\sum_c n_c r_{j,c} \right) \right] + \\
& + \left(r_{1,c} + r_{2m,c} \right) \left(x_s + \lambda_1 x \right) - \xi - \sum_{i=1}^{2m} \zeta_i r_{i,c} = 0
\end{aligned} \tag{27}$$

for all c

$$\left. \frac{\partial F_f}{\partial n_i^0} \right|_{n_c, n_{k \neq i}, \zeta_k, \xi} = - \ln n_i^0 - \zeta_i = 0 \quad 1 \leq i \leq 2m \quad (28)$$

$$\left. \frac{\partial F_f}{\partial \zeta_i} \right|_{n_c, n_k^0, \zeta_{k \neq i}, \xi} = \sum_c n_c r_{i,c} + n_i^0 - L = 0 \quad 1 \leq i \leq 2m \quad (11)$$

$$\left. \frac{\partial F_f}{\partial \xi} \right|_{n_c, n_i^0, \zeta_i} = \sum_c n_c - n_f = 0 \quad (12)$$

Our intention is to solve the system of Eqs. (27), (28), (11) and (12) for the conformation distribution $\{n_c\}$. Once this is obtained, the void distribution is immediately determined from Eq. (11).

We introduce the volume fractions of polymer in each layer:

$$\varphi_i = \frac{1}{L} \sum_c n_c r_{i,c} \quad (29)$$

and the "site volume fractions"¹

$$\langle \varphi_i \rangle = \sum_{j=1}^{2m} \lambda_{j-i} \varphi_j \quad (30)$$

where the quantities λ_{j-i} are defined through Eq. (15).

Eqs. (11) and (29) give:

$$n_i^0 = L \left[1 - \varphi_i \right] \quad (31)$$

Summing Eq. (11) over all layers and using Eqs. (12) and (31), we obtain:

$$\sum_c n_c \left(\sum_{i=1}^{2m} r_{i,c} \right) + L \sum_{i=1}^{2m} \left(1 - \varphi_i \right) - 2mL = 0, \text{ or } L \sum_{i=1}^{2m} \varphi_i = n_f r \quad (32)$$

From Eqs.(28) and (31):

$$\zeta_i = - \ln L - \ln \left(1 - \varphi_i \right) \quad (33)$$

Using Eqs.(29), (30) and (33) in Eq.(27), we obtain:

$$\begin{aligned} & - \ln \left(\frac{n_c}{\omega_c} \right) - \frac{\epsilon_c}{kT} + 2\chi \sum_{i=1}^{2m} r_{i,c} \langle \varphi_i \rangle + \left(r_{1,c} + r_{2m,c} \right) \left(\chi_s + \lambda_1 \chi \right) + \\ & + \sum_{i=1}^{2m} r_{i,c} \ln \left(1 - \varphi_i \right) + \left(\sum_{i=1}^{2m} r_{i,c} \right) \ln L - \xi = 0, \text{ or} \\ n_c = & \exp \left[-\xi + r \ln L \right] \left\{ \omega_c \exp \left[-\frac{\epsilon_c}{kT} \right] \right\} \exp \left[\sum_{i=1}^{2m} r_{i,c} \left\{ \ln \left(1 - \varphi_i \right) + 2\chi \langle \varphi_i \rangle + \left(\delta_{i,1} + \delta_{1,2m} \right) \left(\lambda_1 \chi + \chi_s \right) \right\} \right] \end{aligned} \quad (34)$$

Eq.(34) expresses the distribution of conformations, according to the maximum term approximation. The prefactor $\exp \left[-\xi + r \ln L \right]$ is conformation-independent. The factor $\omega_c \exp \left[-\epsilon_c / (kT) \right]$ is purely intramolecular, i.e. proportional to the probability of occurrence of conformation c in the isolated unperturbed state. The last factor (exponential) incorporates all contributions from excluded volume effects, chain-chain and chain-surface interactions in the multichain

system.

Following Scheutjens and Fleer¹ we will use the term "free segment probability" to denote the quantity P_i , defined by:

$$\ln P_i = \ln[1 - \phi_i] + 2\chi \langle \phi_i \rangle + \left[\delta_{i,1} + \delta_{i,2m} \right] \left[\chi_s + \lambda_1 \chi \right] \quad (35)$$

The term "probability" is somewhat misleading⁸; the quantity P_i is not constrained to vary between 0 and 1. It is rather a Boltzmann factor, incorporating excluded volume, nonbonded interaction and segment-surface interaction effects. This factor is contributed to the probability of occurrence of a conformation by each segment of that conformation that belongs to layer i .

The conformation distribution, Eq.(34), becomes:

$$\begin{aligned} n_c &= \exp\left[-\xi + r \ln L\right] \left\{ \omega_c \exp\left[-\frac{\epsilon}{kT}\right] \right\} \prod_{i=1}^{2m} P_i^{r, c} \\ &= \exp\left[-\xi + r \ln L\right] \left\{ \omega_c \exp\left[-\frac{\epsilon}{kT}\right] \right\} \prod_{s=1}^r P_{k(s, c)} \end{aligned} \quad (36)$$

The product over all successive segments of the chain, that appears in the conformation distribution (36), is characteristic of a "site" lattice model⁸.

Combining Eqs.(12) and (36) we obtain a normalization condition for the prefactor $\exp\left[-\xi + r \ln L\right]$:

$$\exp\left[-\xi + r \ln L\right] \sum_c \left\{ \omega_c \exp\left[-\frac{\epsilon}{kT}\right] \prod_{i=1}^{2m} P_i^{r, c} \right\} = n_f \quad (37)$$

With the conformation distribution, Eq.(36), the availability of the interfacial polymer [Eq.(22)] becomes:

$$\begin{aligned} \frac{1}{kT} \gamma_f(T, P_b, n_f, a, h) = n_f \left\{ (r-1)(1-\ln z) + [-\xi + (r-1)\ln L] \right\} + \\ + 2L \sum_{i=1}^m \left\{ x \phi_i \langle \phi_i \rangle + \ln \left[1 - \phi_i \right] \right\} + 2mL \left(\frac{P_b v^*}{RT} \right) \end{aligned} \quad (38)$$

A detailed derivation of Eq.(38) is given in Appendix A. Eq.(38) provides a particularly simple expression for the availability of the interfacial polymer in terms of L , the volume fraction distribution $\{\phi_i\}$ and the Lagrange multiplier ξ . The number of chains, n_f , can be obtained from L and the ϕ_i profile through Eq.(32). It is remarkable that an explicit consideration of conformations is not required for calculating γ_f .

As mentioned above, the microscopic degree of freedom L (equivalently, the surface area a wetted by the n_f interfacial chains on either plate) is still free in our expression for γ_f . This degree of freedom will be fixed in the global thermodynamic formulations of sections III and IV. These formulations will require the derivative of γ_f with respect to L , keeping all other microscopic degrees of freedom constant, and evaluated at the optimal distribution of interfacial conformations. A detailed calculation of this derivative is presented in Appendix B. The result is:

$$\begin{aligned}
\left. \frac{1}{kT} \frac{\partial \gamma_f}{\partial L} \right|_{\{n_c\}, T, P_b, h} &= \frac{a^*}{RT} \left. \frac{\partial \gamma_f}{\partial a} \right|_{T, P_b, n_f, h} = \\
&= 2 \left(1 - \frac{1}{r} \right) \sum_{i=1}^m \varphi_i + 2 \sum_{i=1}^m \left\{ x \varphi_i \langle \varphi_i \rangle + \ln(1 - \varphi_i) \right\} + 2m \left(\frac{P_b v^*}{RT} \right)
\end{aligned} \tag{39}$$

B. Conformation Propagation and Segment Balance Equations in the Interfacial Polymer

According to Eq.(38) the availability of the interfacial polymer can be obtained, if the number of surface sites L , the Lagrange multiplier ξ and the volume fractions of polymer in successive layers, φ_i , are known. Here we will develop a set of equations for the self-consistent determination of the volume fraction profile $\{\varphi_i\}$, given the values of L and ξ and the molecular characteristics of the system. This set of equations stems directly from the conditions (27), (28), (11) and (12), that govern the interfacial polymer, and can be solved without explicit consideration of conformations in the interfacial region. The formulation presented here is an extension of techniques used in the Scheutjens and Fleer model of polymer solutions.¹

In view of the conformation distribution, Eq.(36), and Eqs.(9) and (18), we define the (unnormalized) "conformation probability" $P(r)_c$ for conformation c as:

$$P(r)_c = \omega_c \exp\left[-\frac{\epsilon c}{kT}\right] \prod_{s=1}^r P_{k(s,c)} =$$

$$= \left[\prod_{s=1}^{r-1} \left(\lambda_{s,s+1} \right)_c \right] \left[\prod_{s=1}^{r-2} \exp \left\{ - \frac{1}{kT} \epsilon \left[k(s+1,c) - k(s,c), k(s+2,c) - k(s+1,c) \right] \right\} \right] \left[\prod_{s=1}^r P_{k(s,c)} \right] \quad (40)$$

We proceed further exactly as in Ref.8, defining the "chain probability"

$$P(r) = \sum_c P(r)_c \quad (41)$$

The probability that the s^{th} segment of a chain in conformation c belong to layer i is defined as:

$$P(s,i;r)_c = \begin{cases} P(r)_c, & \text{if } k(s,c)=i \\ 0, & \text{otherwise} \end{cases} \quad (42)$$

and the probability of finding the s^{th} segment of any chain in layer i is:

$$P(s,i;r) = \sum_c P(s,i;r)_c \quad (43)$$

By Eqs.(41),(42) the latter fulfils the normalization:

$$\sum_{i=1}^M P(s,i;r) = \sum_c \sum_{i=1}^M P(s,i;r)_c = \sum_c P(r)_c = P(r) \quad (44)$$

We define the "end segment probability" as:

$$P(i,r) \equiv P(r,i;r) \quad (45)$$

This also fulfils the normalization, Eq.(44). End segment probabilities for subchains of length s ($1 \leq s \leq r$) are defined by complete analogy to $P(i,r)$. The quantity $P(i,s)$ is proportional to the likelihood that a subchain s segments long, starting anywhere

in the lattice, have its s^{th} segment in layer i . We will use the symbol $c(s)$ to denote the conformations accessible to a subchain of s segments.

Our objective now is to deduce a recursive relationship, connecting the end segment probabilities $P(i,s)$ with those of shorter subchains. By the definitions, Eqs.(40) through (45), taken with s in place of r :

$$\begin{aligned}
 P(i,s) &= P(s,i;s) = \sum_{c(s)} P(s,i;s)_{c(s)} = \sum_{c(s)} P(s)_{c(s)} \delta_{i,k(s,c(s))} = \\
 &= \sum_{c(s)} \left\{ \left[\prod_{t=1}^{s-1} \left(\lambda_{t,t+1} \right)_{c(s)} \right] \left[\prod_{t=1}^{s-2} \exp \left(-\frac{1}{kT} \left[k(t+1,c(s)) - k(t,c(s)), k(t+2,c(s)) - k(t+1,c(s)) \right] \right) \right] \right\} \\
 &\quad \left\{ \left[\prod_{t=1}^s P_{k(t,c(s))} \right] \delta_{i,k(s,c(s))} \right\} \quad (46)
 \end{aligned}$$

Now, if segment s lies in layer i , segment $(s-1)$ must necessarily lie in one of the layers $i-1$, i or $i+1$. Symbolically:

$$\begin{aligned}
 \sum_{c(s)} \delta_{i,k(s,c(s))} &= \\
 &= \delta_{i,k(s,c(s))} \sum_{c(s-1)} \left\{ \delta_{i-1,k(s-1,c(s-1))} + \delta_{i,k(s-1,c(s-1))} + \delta_{i+1,k(s-1,c(s-1))} \right\} \quad (47)
 \end{aligned}$$

Using Eq.(47) in Eq.(46) we obtain:

$$\begin{aligned}
P(i, s) = & P_i \left\{ \lambda_1 \sum_{c(s-1)} \left\{ \exp \left\{ -\frac{1}{kT} \epsilon \left[(i-1) - k(s-2, c(s-1)), +1 \right] \right\} \left[\prod_{t=1}^{s-2} (\lambda_{t, t+1})_{c(s-1)} \right] \right. \right. \\
& \left. \left[\prod_{t=1}^{s-3} \exp \left\{ -\frac{1}{kT} \epsilon \left[k(t+1, c(s-1)) - k(t, c(s-1)), k(t+2, c(s-1)) - k(t+1, c(s-1)) \right] \right\} \right] \right. \\
& \left. \left[\prod_{t=1}^{s-1} P_{k(t, c(s-1))} \right] \delta_{i-1, k(s-1, c(s-1))} \right\} + \\
& + \lambda_0 \sum_{c(s-1)} \left\{ \exp \left\{ -\frac{1}{kT} \epsilon \left[i - k(s-2, c(s-1)), 0 \right] \right\} \left[\prod_{t=1}^{s-2} (\lambda_{t, t+1})_{c(s-1)} \right] \right. \\
& \left. \left[\prod_{t=1}^{s-3} \exp \left\{ -\frac{1}{kT} \epsilon \left[k(t+1, c(s-1)) - k(t, c(s-1)), k(t+2, c(s-1)) - k(t+1, c(s-1)) \right] \right\} \right] \right. \\
& \left. \left[\prod_{t=1}^{s-1} P_{k(t, c(s-1))} \right] \delta_{i, k(s-1, c(s-1))} \right\} + \\
& + \lambda_1 \sum_{c(s-1)} \left\{ \exp \left\{ -\frac{1}{kT} \epsilon \left[(i+1) - k(s-2, c(s-1)), -1 \right] \right\} \left[\prod_{t=1}^{s-2} (\lambda_{t, t+1})_{c(s-1)} \right] \right. \\
& \left. \left[\prod_{t=1}^{s-3} \exp \left\{ -\frac{1}{kT} \epsilon \left[k(t+1, c(s-1)) - k(t, c(s-1)), k(t+2, c(s-1)) - k(t+1, c(s-1)) \right] \right\} \right] \right. \\
& \left. \left[\prod_{t=1}^{s-1} P_{k(t, c(s-1))} \right] \delta_{i+1, k(s-1, c(s-1))} \right\} \Bigg\}
\end{aligned}
\tag{48}$$

The chain conformations involved in the decomposition, Eq.(48), are pictorially represented in Fig.3.

To establish a recursive relation between end segment probabilities, we need to factor the exponentials appearing on the right of the summation signs in Eq.(48) out of the respective summations. Except for the case of freely jointed chains (no conformational energy contribution), this is strictly not possible, because these exponentials depend on the position of segment (s-2). To proceed, we introduce a preaveraging approximation, rewriting Eq.(48) as follows:

$$\begin{aligned}
 P(i,s) = & P_i \left\{ \lambda_1 \left\langle \exp \left[-\frac{1}{kT} \epsilon \left[(i-1) - k(s-2, c(s-2)), +1 \right] \right] \right\rangle_{\substack{c(s-2): \\ k(s-1, \\ c(s-1)) = \\ = (i-1)}} \sum_{c(s-1)} \left\{ \prod_{t=1}^{s-2} (\lambda_{t,t+1})_{c(s-1)} \right\} \\
 & \left[\prod_{t=1}^{s-3} \exp \left[-\frac{1}{kT} \epsilon \left[k(t+1, c(s-1)) - k(t, c(s-1)), k(t+2, c(s-1)) - k(t+1, c(s-1)) \right] \right] \right] \\
 & \left[\prod_{t=1}^{s-1} P_{k(t, c(s-1))} \right] \delta_{i-1, k(s-1, c(s-1))} \Bigg\} + \\
 & + \lambda_0 \left\langle \exp \left[-\frac{1}{kT} \epsilon \left[i - k(s-2, c(s-2)), 0 \right] \right] \right\rangle_{\substack{c(s-2): \\ k(s-1, \\ c(s-1)) = i}} \sum_{c(s-1)} \left\{ \prod_{t=1}^{s-2} (\lambda_{t,t+1})_{c(s-1)} \right\} \\
 & \left[\prod_{t=1}^{s-3} \exp \left[-\frac{1}{kT} \epsilon \left[k(t+1, c(s-1)) - k(t, c(s-1)), k(t+2, c(s-1)) - k(t+1, c(s-1)) \right] \right] \right] \\
 & \left[\prod_{t=1}^{s-1} P_{k(t, c(s-1))} \right] \delta_{i, k(s-1, c(s-1))} \Bigg\} +
 \end{aligned}$$

$$\begin{aligned}
& + \lambda_1 \left\langle \exp \left\{ -\frac{1}{kT} \epsilon \left[(i+1) - k(s-2, c(s-2)), -1 \right] \right\} \right\rangle_{\substack{c(s-2): \\ k(s-1, \\ c(s-1))=i+1}} \sum_{c(s-1)} \left\{ \left[\prod_{t=1}^{s-2} (\lambda_{t,t+1})_{c(s-1)} \right] \right. \\
& \left. \left[\prod_{t=1}^{s-3} \exp \left\{ -\frac{1}{kT} \epsilon \left[k(t+1, c(s-1)) - k(t, c(s-1)), k(t+2, c(s-1)) - k(t+1, c(s-1)) \right] \right\} \right] \right. \\
& \left. \left[\prod_{t=1}^{s-1} P_{k(t, c(s-1))} \right] \delta_{i+1, k(s-1, c(s-1))} \right\} \Bigg] \quad (49)
\end{aligned}$$

The sums in Eq.(49) have now been reduced to end segment probabilities of (s-1)-long subchains [compare Eq.(46)]. The averages of the Boltzmann factors in Eq.(49) are taken over all conformations of (s-2)-long subchains, that are compatible with the position of segment (s-1). Setting

$$\left. \begin{aligned} \tau_L &= \exp \left\{ -\frac{\epsilon_L}{kT} \right\} \\ \tau_V &= \exp \left\{ -\frac{\epsilon_V}{kT} \right\} \end{aligned} \right\} \quad (50)$$

and taking into account all conformational possibilities depicted in Fig.3, we express these averages as:

$$\begin{aligned}
& \left\langle \exp \left\{ -\frac{1}{kT} \epsilon \left[(i-1) - k(s-2, c(s-2)), +1 \right] \right\} \right\rangle_{c(s-2): k(s-1, c(s-1))=(i-1)} = \\
& = \frac{\lambda_1 P(i-2, s-2) + \lambda_0 \tau_L P(i-1, s-2) + \lambda_1 \tau_V P(i, s-2)}{\lambda_1 P(i-2, s-2) + \lambda_0 P(i-1, s-2) + \lambda_1 P(i, s-2)}
\end{aligned}$$

$$\begin{aligned}
& \left\langle \exp \left[-\frac{1}{kT} \epsilon \left[i-k(s-2, c(s-2)), 0 \right] \right] \right\rangle_{c(s-2):k(s-1, c(s-1))=i} = \\
& = \frac{\lambda_1 \tau_L P(i-1, s-2) + [(\lambda_0 - 2\lambda_1) \tau_L + \lambda_1 \tau_V + \lambda_1] P(i, s-2) + \lambda_1 \tau_L P(i+1, s-2)}{\lambda_1 P(i-1, s-2) + \lambda_0 P(i, s-2) + \lambda_1 P(i+1, s-2)} = \\
& \left\langle \exp \left[-\frac{1}{kT} \epsilon \left[(i+1)-k(s-2, c(s-2)), -1 \right] \right] \right\rangle_{c(s-2):k(s-1, c(s-1))=(i+1)} = \\
& = \frac{\lambda_1 \tau_V P(i, s-2) + \lambda_0 \tau_L P(i+1, s-2) + \lambda_1 P(i+2, s-2)}{\lambda_1 P(i, s-2) + \lambda_0 P(i+1, s-2) + \lambda_1 P(i+2, s-2)}
\end{aligned} \tag{51}$$

In the case of a freely jointed chain all averages in Eq. (51) reduce to unity. In the general case there is no conformational energy associated with going from an $s=1$ to an $s=2$ long subchain. A simpler recursive relationships holds for this first step, exactly as in the case of freely jointed chains⁸. With these observations, we can cast the recursive relations (49) in matrix form, as follows:

$$\begin{bmatrix} P(1,s) \\ P(2,s) \\ \vdots \\ P(i,s) \\ \vdots \\ P(m-1,s) \\ P(m,s) \end{bmatrix} = \begin{bmatrix} \lambda_0 H^0(1,s) P_1 & \lambda_1 H^-(1,s) P_1 & 0 & \cdot & \cdot & \cdot & 0 \\ \lambda_1 H^+(2,s) P_2 & \lambda_0 H^0(2,s) P_2 & \lambda_1 H^-(2,s) P_2 & \cdot & \cdot & \cdot & \cdot \\ 0 & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \lambda_1 H^+(i,s) P_i & \lambda_0 H^0(i,s) P_i & \lambda_1 H^-(i,s) P_i & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & 0 \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ P(m-1,s) & \cdot & \cdot & \cdot & \lambda_1 H^+(m-1,s) P_{m-1} & \lambda_0 H^0(m-1,s) P_{m-1} & \lambda_1 H^-(m-1,s) P_{m-1} \\ P(m,s) & 0 & \cdot & \cdot & 0 & \lambda_1 H^0(m,s) P_m & \left[\lambda_0 H^0(m,s) + \lambda_1 H^-(m,s) \right] P_m \end{bmatrix} \begin{bmatrix} P(1,s-1) \\ P(2,s-1) \\ \vdots \\ P(i,s-1) \\ \vdots \\ P(m-1,s-1) \\ P(m,s-1) \end{bmatrix}$$

$$2 \leq s \leq r$$

$$(52)$$

where

$$\left. \begin{array}{l} P(i,1) = P_i \quad 1 \leq i \leq m \\ P(-1,s) = P(0,s) = 0 \\ P(m+1,s) = P(m,s); \quad P(m+2,s) = P(m-1,s) \end{array} \right\} \quad \begin{array}{l} 2 \leq s \leq r \end{array} \quad (53)$$

and

$$\left. \begin{array}{l} H^+(i,2) = H^0(i,2) = H^-(i,2) = 1 \\ H^+(i,s) = \frac{\lambda_1 P(i-2,s-2) + \lambda_0 \tau_L P(i-1,s-2) + \lambda_1 \tau_V P(i,s-2)}{\lambda_1 P(i-2,s-2) + \lambda_0 P(i-1,s-2) + \lambda_1 P(i,s-2)} \\ H^0(i,s) = \frac{\lambda_1 \tau_L P(i-1,s-2) + \left[(\lambda_0 - 2\lambda_1) \tau_L + \lambda_1 \tau_V + \lambda_1 \right] P(i,s-2) + \lambda_1 \tau_L P(i+1,s-2)}{\lambda_1 P(i-1,s-2) + \lambda_0 P(i,s-2) + \lambda_1 P(i+1,s-2)} \\ H^-(i,s) = \frac{\lambda_1 \tau_V P(i,s-2) + \lambda_0 \tau_L P(i-1,s-2) + \lambda_1 P(i+2,s-2)}{\lambda_1 P(i,s-2) + \lambda_0 P(i+1,s-2) + \lambda_1 P(i+2,s-2)} \end{array} \right\} \quad \begin{array}{l} 1 \leq i \leq m, \quad 3 \leq s \leq r \end{array} \quad (54)$$

In writing Eqs.(52) we have confined ourselves to half the interfacial domain depicted in Fig.1, and employed the symmetry⁸ with respect to the midplane separating layers m and $(m+1)$. Eqs.(52) provide a convenient second order recursive scheme for obtaining all end segment probabilities from free segment probabilities, hence [see Eq.(35)] from the polymer volume fraction profile. We will refer to them as the "conformation propagation equations".

We emphasize that the treatment of intramolecular (conformational) energy in this model is approximate: It is based on a simple molecular representation; it ignores second order interactions (such as the pentane effect); it invokes a layerwise mean field treatment and a preaveraging approximation; also, it is strictly Markovian, and thus ignores the bidirectional nature of

chain conformational statistics¹².

The introduction of end segment probabilities makes it possible to recast the segment balance Eqs.(11) in a form that does not require consideration of individual chain conformations. We have not yet fully exploited the information content of these equations. Combining Eqs.(11),(13),(31),(36) and (40) we obtain:

$$\begin{aligned} \exp(\xi - r \ln L) L \varphi_i &= \exp(\xi - r \ln L) \sum_c r_{i,c} n_c = \sum_c r_{i,c} P(r)_c = \\ &= \sum_c \left\{ \sum_{s=1}^r \delta_{i,k(s,c)} \right\} P(r)_c = \sum_{s=1}^r \left\{ \sum_c \delta_{i,k(s,c)} P(r)_c \right\} \end{aligned} \quad (55)$$

By the definitions, Eqs.(42) and (43) we can further write:

$$\begin{aligned} \exp[\xi - (r-1) \ln L] \varphi_i &= \sum_{s=1}^r \left\{ \sum_c P(s,i;r)_c \right\} = \sum_{s=1}^r P(s,i;r) , \text{ or} \\ \varphi_i &= \exp[-\xi + (r-1) \ln L] \sum_{s=1}^r P(s,i;r) \end{aligned} \quad (56)$$

Our objective now is to express the quantity $P(s,i;r)$ in terms of end segment probabilities. To accomplish this^{1,8} we consider a chain having its s^{th} segment in layer i as the sum of two subchains, of lengths s and $(r-s+1)$ segments, sharing a common terminal segment in layer i (see Fig.4.) In view of the product form of the conformation probability distribution, Eq.(40):

$$\begin{aligned}
P(s,i;r) &= \sum_c P(r)_c \delta_{i,k(s,c)} = \\
&= \frac{1}{P_i} \sum_{c(s)} \sum_{c(r-s+1)} P(s)_{c(s)} \delta_{i,k(s,c(s))} P(r-s+1)_{c(r-s+1)} \delta_{i,k(r-s+1,c(r-s+1))} \\
&\quad \exp\left\{-\frac{1}{kT} \epsilon\left[i-k(s-1,c(s)),k(r-s,c(r-s+1))-i\right]\right\}
\end{aligned} \tag{57}$$

In Eq. (57) the summation over all conformations of an r -long chain passing through layer i has been replaced by a double summation over all conformations of an s -long subchain and a $(r-s+1)$ -long subchain, both terminating in layer i . The division by P_i corrects for the fact that the free segment probability of the common segment is doublecounted. It is desired to factor Eq. (57) into a product of two sums. Such a factorization is strictly not possible, owing to the appearance of the conformational energy exponential, which depends on the locations of the penultimate segments of the two subchains. To proceed, we introduce again a preaveraging approximation, writing Eq. (57) as:

$$\begin{aligned}
P(s,i;r) &= \frac{1}{P_i} P(i,s) P(i,r-s+1) \\
&\quad \left\langle \exp\left\{-\frac{1}{kT} \epsilon\left[i-k(s-1,c(s-1)),k(r-s,c(r-s))-i\right]\right\} \right\rangle_{\substack{c(s-1) \\ c(r-s) \\ k(s,c(s))= \\ =k(r-s+1,c(r-s+1))=i}}
\end{aligned} \tag{58}$$

The average in Eq.(58) is taken over all possible pairs of (s-1)- and (r-s)- subchain conformations, compatible with the requirement that each pair be joinable by two bonds, both emanating from the same site in layer i. Fig.3, with all segment indices increased by 1, and with layer numbers reindexed so that layer i lies in the middle, is useful in visualizing the possible arrangements of these subchain conformations.

We estimate the average in Eq.(58) as:

$$\begin{aligned}
 & \left\langle \exp \left[-\frac{1}{kT} \epsilon \left[i - k(s-1, c(s-1)), k(r-s, c(r-s)) - 1 \right] \right] \right\rangle_{\substack{c(s-1) \\ c(r-s) \\ k(s, c(s)) = k(r-s+1, c(r-s+1)) = i}} = \\
 & \equiv Y(i, s) = \\
 & = \frac{1}{\left[\lambda_1 P(i-1, s-1) + \lambda_0 P(i, s-1) + \lambda_1 P(i+1, s-1) \right] \left[\lambda_1 P(i-1, r-s) + \lambda_0 P(i, r-s) + \lambda_1 P(i+1, r-s) \right]} \\
 & \left\{ \lambda_1^2 P(i-1, s-1) P(i-1, r-s) \tau_V + \lambda_1 \lambda_0 P(i-1, s-1) P(i, r-s) \tau_L + \lambda_1^2 P(i-1, s-1) P(i+1, r-s) + \right. \\
 & + \lambda_0 \lambda_1 P(i, s-1) P(i-1, r-s) \tau_L + \lambda_0 \left[\lambda_1 \tau_V + (\lambda_0 - 2\lambda_1) \tau_L + \lambda_1 \right] P(i, s-1) P(i, r-s) + \\
 & + \lambda_0 \lambda_1 P(i, s-1) P(i+1, r-s) \tau_L + \lambda_1^2 P(i+1, s-1) P(i-1, r-s) + \lambda_1 \lambda_0 P(i+1, s-1) P(i, r-s) \tau_L + \\
 & \left. + \lambda_1^2 P(i+1, s-1) P(i+1, r-s) \tau_V \right\} \\
 & \qquad \qquad \qquad 1 \leq i \leq m \\
 & \qquad \qquad \qquad 2 \leq s \leq r-1
 \end{aligned} \tag{59}$$

No additional intramolecular energy contribution is introduced in considering a chain as a sum of itself and a monomer located at either of its ends. In this case the averaged Boltzmann factor of Eq.(58) is equal to unity:

$$Y(i, 1) = Y(i, r) = 1 \tag{60}$$

Combining Eqs.(56) and (58) we can write the segment balance equations as:

$$\phi_i = \exp[-\xi + (r-1)\ln L] \frac{1}{P_i} \sum_{s=1}^r P(i,s) P(i,r-s+1) Y(i,s) \quad (61)$$

$1 \leq i \leq m$

where the factors Y are defined in Eqs.(59) and (60).

For a given value of the prefactor $\exp[-\xi + (r-1)\ln L]$ the m segment balance Eqs.(61), together with the recursive conformation propagation Eqs.(52) and the definitions, Eqs.(53), (54), (60) and (61), comprise a system that can be solved for the m volume fractions ϕ_i , $1 \leq i \leq m$. Thus, closure of our interfacial model amounts to determining the quantity $-\xi + (r-1)\ln L$. This determination is accomplished in Sections III and IV of this paper. Note that, since strictly intensive properties are involved in the segment balance and conformation propagation equations, the quantity $-\xi + (r-1)\ln L$ is expected to be an intensive property of the model system.

C. Availability of the Bulk Polymer

A molecular thermodynamic description of the unconstrained bulk polymer is needed for formulating the conditions of global equilibrium in the system considered in Fig.1. Our statistical mechanical analysis here follows the work of Sanchez and Lacombe⁶. Consider n_b / N_L moles of the bulk lattice polymer at temperature T and pressure P_b . In configuration space the system is completely specified by fixing the conformations and positions of the n_b chains

comprising it, as well as the positions of the n_b^o voids it contains. At equilibrium the system is uniform. The random mixing approximation (Assumption 3) is used in laying down chains in all three directions; no distinction is made among different sites or layers in the lattice. With this approximation the microscopic degrees of freedom reduce to the total number of voids n_b^o , and the conformational distribution of chains, denoted symbolically by $\{n_c\}$. Specifying $\{n_c\}$ amounts to specifying the relative orientations of all pairs of adjacent bonds for all chains in the system. In our mean field treatment the energy of a microstate $\{n_b^o, \{n_c\}\}$ consists of segment-segment interaction and intramolecular contributions:

$$\begin{aligned} E_b(n_b^o, \{n_c\}) &= E_{b,AA}(n_b^o) + E_{intra}(\{n_c\}) = \\ &= \frac{1}{2} (n_b r) z \left(\frac{n_b r}{n_b r + n_b^o} \right) w_{AA} + \sum_c n_c \epsilon_c \end{aligned} \quad (62)$$

The microstates of the bulk polymer are degenerate. The number of ways, in which the microstate $\{n_b^o, \{n_c\}\}$ can be realized, is written as:

$$\begin{aligned} \Omega_b(n_b^o, \{n_c\}) &= \Omega_{b,fj}(n_b^o) \frac{\Omega_b^{intra}(\{n_c\})}{\Omega_{b,fj}^{intra}} = \\ &= \left(\frac{n_b r + n_b^o}{n_b^o} \right)^{n_b^o} \left[\frac{r z^{r-1}}{e^{r-1}} \frac{n_b r + n_b^o}{n_b r} \right]^{n_b} \frac{\Omega_b^{intra}(\{n_c\})}{\Omega_{b,fj}^{intra}} \end{aligned} \quad (63)$$

In Eq. (63) the quantity $\Omega_{b,fj}$ is the number of ways in which n_b^o voids and n_b freely jointed chains can be arranged in the lattice^{6,9}.

$\Omega_{b,fj}$ has been estimated using the random mixing approximation in

all three directions, in its large coordination number, or "Flory" form (Assumption 3). Chain backstepping has been allowed in this estimation, for consistency with the interfacial analysis of Section II.A. Note that our $\Omega_{b,fj}$ is identical to that used in Sanchez and Lacombe's work⁶ for a "flexibility parameter" equal to z^{r-1} and a "symmetry number" equal to 1. The quantity Ω_b^{intra} stands for the number of ways in which a set of n_b single chain conformations, that obeys the distribution $\{n_c\}$, can be generated. It depends solely on geometrical characteristics of individual conformations, and not on interchain effects. Correspondingly, $\Omega_{b,fj}^{\text{intra}}$ is the number of ways in which one can generate n_b freely jointed chain conformations. Division by $\Omega_{b,fj}^{\text{intra}}$ in Eq.(63) is necessary, because $\Omega_{b,fj}^{\text{intra}}$ is already incorporated in $\Omega_{b,fj}$, by construction. The ratio $\Omega_b^{\text{intra}}/\Omega_{b,fj}^{\text{intra}}$ in Eq.(63) will account for the fact that our lattice chains are not freely jointed, but there is a potential energy contribution associated with their conformation.

The availability of the bulk polymer is coincident with its Gibbs energy, since pressure is uniform in the bulk phase. The configurational part of the availability is obtained within the formalism of the isothermal-isobaric ensemble as:

$$\bar{r}_b(T, P_b, n_b) = -kT \ln \left\{ \sum_{n_b^0=0}^{\infty} \sum_{\{n_c\}} \Omega_b(n_b^0, \{n_c\}) \exp \left[-\frac{1}{kT} \left[E_b(n_b^0, \{n_c\}) + P_b \frac{v^*}{N_L} (n_b r + n_b^0) \right] \right] \right\} \quad (64)$$

In view of Eqs.(62) and (63) the isothermal-isobaric partition

function can be factored, and the availability separated into two terms:

$$\begin{aligned} \underline{r}_b(T, P_b, n_b) = & -kT \ln \left\{ \sum_{n_b^o=0}^{\infty} \Omega_{b,fj}(n_b^o) \exp \left\{ -\frac{1}{kT} \left[E_{b,AA}(n_b^o) + \frac{P_b v^*}{N_L} (n_b r + n_b^o) \right] \right\} \right\} - \\ & -kT \ln \left\{ \frac{1}{\Omega_{b,fj}^{intra}} \sum_{\{n_c\}} \Omega_b^{intra}(\{n_c\}) \exp \left\{ -\frac{1}{kT} \sum_c n_c \epsilon_c \right\} \right\} \end{aligned} \quad (65)$$

Intermolecular and long-range intramolecular interactions are completely decoupled from short-range intramolecular energetics in our treatment of the bulk polymer (random coil hypothesis⁹).

We will use a maximum term approximation to estimate the first (n_b^o -dependent) part of the availability function, writing:

$$\begin{aligned} \underline{r}_b(T, P_b, n_b) = & -kT \ln \left\{ \Omega_{b,fj}(n_b^o) \exp \left\{ -\frac{1}{kT} \left[E_{b,AA}(n_b^o) + \frac{P_b v^*}{N_L} (n_b r + n_b^o) \right] \right\} \right\} - \\ & -kT \ln \left\{ \frac{1}{\Omega_{b,fj}^{intra}} \sum_{\{n_c\}} \Omega_b^{intra}(\{n_c\}) \exp \left\{ -\frac{1}{kT} \sum_c n_c \epsilon_c \right\} \right\} \end{aligned} \quad (66)$$

where n_b^o is the solution to the optimization problem:

$$\text{Maximize} \quad \ln \Omega_{b,fj}(n_b^o) - \frac{1}{kT} E_{b,AA}(n_b^o) - \frac{P_b v^*}{RT} (n_b r + n_b^o) \quad (67)$$

with respect to n_b^o , subject to the macroscopic constraints existing between phase b and its environment.

This optimization will be performed in Section III of this paper. For

convenience, we will use the polymer volume fraction in the bulk in place of n_b^0 :

$$\phi_b = \frac{n_b r}{n_b r + n_b^0} \quad (68)$$

The quantity ϕ_b is related to the volume of the bulk polymer phase by:

$$\underline{v}_b = \frac{n_b}{N_L} \frac{r v^*}{\phi_b} \quad (69)$$

The second (conformational) part of the availability we calculate as follows:

We first reduce the sum over all conformation distributions to a sum over all conformations of a single chain. Since the conformations of different chains in the intramolecular terms are not coupled energetically, we can write, treating each individual chain as a distinguishable entity:

$$\frac{1}{\Omega_{b,fj}^{intra}} \sum_{\{n_c\}} \Omega_b^{intra}(\{n_c\}) \exp\left[-\frac{1}{kT} \sum_c n_c \epsilon_c\right] = \quad (70)$$

$$= \frac{1}{\Omega_{b,fj}^{intra}} \sum_{\substack{c_1 \\ \text{all} \\ \text{conformations} \\ \text{of chain 1}}} \cdot \cdot \cdot \sum_{\substack{c_{n_b} \\ \text{all} \\ \text{conformations} \\ \text{of chain } n_b}} \exp\left[-\frac{1}{kT} (\epsilon_{c_1} + \epsilon_{c_2} + \dots + \epsilon_{c_n})\right]$$

In Eq.(70) c_k stands for the conformation assumed by chain k , and ϵ_{c_k} is the intramolecular energy characteristic of that conformation.

The right hand side of Eq.(70) is further written as:

$$\begin{aligned}
\frac{1}{\Omega_{b,fj}^{intra}} \sum_{\{c_1, c_2, \dots, c_{n_b}\}} \left\{ \prod_{k=1}^{n_b} \exp \left[-\frac{\epsilon_c}{kT} \right] \right\} &= \frac{1}{\Omega_{b,fj}^{intra}} \prod_{k=1}^{n_b} \sum_{c_k} \exp \left[-\frac{\epsilon_c}{kT} \right] = \\
&= \frac{1}{\Omega_{b,fj}^{intra}} \left\{ \sum_c \exp \left[-\frac{\epsilon_c}{kT} \right] \right\}^{n_b}
\end{aligned} \tag{71}$$

Next we calculate the sum of intrachain energy Boltzmann factors over all possible conformations of a single chain, that appears in the last term of Eq.(71). A single chain conformation can be described as an ordered sequence of $(r-2)$ states, characteristic of the relative placement of all bond pairs along the backbone. Consider one such sequence, containing a total of s_L gauche bond pairs, s_V backstepping bond pairs and $(r-2-s_L-s_V)$ trans bond pairs, defined as in Fig.2. This particular sequence can be realized in

$$(\lambda_1 z)^{r-2-s_L-s_V} (\lambda_0 z)^{s_L} (\lambda_1 z)^{s_V} = \lambda_1^{r-2-s_L} \lambda_0^{s_L} z^{r-2} \text{ ways.}$$

Consider now all sequences containing s_L gauche and s_V backstepping bond pairs, irrespective of the location of these bond pairs along the backbone. There are $\frac{(r-2)!}{s_L! s_V! (r-2-s_L-s_V)!}$ such sequences, all characterized by a conformational energy

$$\epsilon_c = s_L \epsilon_L + s_V \epsilon_V \tag{72}$$

Summing over all possible values of s_L and s_V along a chain, we obtain:

$$\begin{aligned}
\sum_c \exp\left(-\frac{\epsilon_c}{kT}\right) &= \sum_{\substack{s_L \geq 0 \\ s_V \geq 0 \\ s_L + s_V \leq r-2}} \sum_{s_V \geq 0} \frac{(r-2)! \lambda_1^{r-2-s_L} \lambda_0^{s_L} z^{r-2}}{s_L! s_V! (r-2-s_L-s_V)!} \left[\exp\left(-\frac{\epsilon_L}{kT}\right)\right]^{s_L} \left[\exp\left(-\frac{\epsilon_V}{kT}\right)\right]^{s_V} = \\
&= z^{r-2} \sum_{s_L \geq 0} \sum_{s_V \geq 0} \sum_{\substack{s_I \geq 0 \\ s_I + s_L + s_V = r-2}} \frac{(r-2)!}{s_I! s_L! s_V!} \lambda_1^{s_I} \left[\lambda_0 \exp\left(-\frac{\epsilon_L}{kT}\right)\right]^{s_L} \left[\lambda_1 \exp\left(-\frac{\epsilon_V}{kT}\right)\right]^{s_V} = \\
&= z^{r-2} \left\{ \lambda_1 + \lambda_0 \tau_L + \lambda_1 \tau_V \right\}^{r-2}
\end{aligned} \tag{73}$$

On the other hand, generating a freely jointed chain involves the successive placement of $(r-2)$ bonds (all bonds except the first) in a z -way lattice, with no energy penalty. Therefore, n_b distinguishable freely jointed chains can be generated in

$$\Omega_{b,fj}^{\text{intra}} = z^{n_b(r-2)} \quad \text{ways.} \tag{74}$$

Combining Eqs. (70), (71), (73) and (74) we obtain:

$$\frac{1}{\Omega_{b,fj}^{\text{intra}}} \sum_{\{n_c\}} \Omega_b^{\text{intra}}(\{n_c\}) \exp\left(-\frac{1}{kT} \sum_c n_c \epsilon_c\right) = \left\{ \lambda_1 + \lambda_0 \tau_L + \lambda_1 \tau_V \right\}^{n_b(r-2)} \tag{75}$$

Furthermore, combining Eqs. (66), (62), (63), (68) and (75) we can write the availability of the bulk polymer as:

$$\begin{aligned} \frac{1}{kT} \underline{r}_b(T, P_b, n_b, V_b) = n_b \left\{ (r-1)(1-\ln z) - \ln r - r\phi_b + r \frac{(1-\phi_b)}{\phi_b} \ln(1-\phi_b) + \ln \phi_b + \right. \\ \left. + \frac{P_b v^*}{RT} \frac{r}{\phi_b} - (r-2) \ln[\lambda_1 + \lambda_o \tau_L + \lambda_1 \tau_V] \right\} \end{aligned} \quad (76)$$

The volume V_b has been inserted among the arguments of $\underline{r}_b$, as a reminder of the fact that a minimization of the availability $\underline{r}_b$ with respect to ϕ_b has not yet been performed. At equilibrium only three of the thermodynamic variables T , P_b , n_b and V_b are independent.

III. THERMODYNAMIC ANALYSIS: FULL EQUILIBRIUM

A. Model Closure

Our statistical mechanical analysis, presented in Section I, has led to an expression for the availability of the interfacial polymer, Eq.(38), which involves the volume fraction profile $\{\phi_i\}$ in the interfacial region and the intensive quantity $-\xi+(r-1)\ln L$; also, to a scheme, Eqs.(52) to (54), (60) and (61), that can be used to calculate the profile $\{\phi_i\}$ for a given value of $-\xi+(r-1)\ln L$; finally, to an expression for the availability of the unconstrained bulk polymer, Eq.(76), that involves the volume fraction of chains in the lattice, ϕ_b . We will now combine these pieces of information in a global thermodynamic formulation, leading to the determination of $-\xi+(r-1)\ln L$ and ϕ_b , hence to closure of our model.

Our analysis here assumes complete thermodynamic equilibrium between the phases s, f and b of Fig.1 ("full equilibrium model").

We concentrate on the thermodynamic system depicted in Fig.5(a). This consists of equal and opposite portions of the two slabs of phase s at temperature T , each having a surface area a , and each containing $n_s/2N_L$ moles of solid (or gas); of the interfacial polymer in between (n_f/N_L moles) at temperature T ; and of a quantity of the surrounding bulk polymer (n_b/N_L moles), at temperature T and pressure P_b . The total quantity of polymer in the system,

$$n = n_f + n_b = \text{const.} \quad (77)$$

is fixed, as is n_s . The quantities n_f and n_b are not fixed a priori; the polymer will be allowed to distribute itself between the interfacial phase and the bulk according to the requirements of equilibrium. The infinitely extending (Assumption 2) bulk polymer phase b acts as a heat (constant T), work (constant P_b) and mass (constant chemical potential) reservoir for the interfacial polymer f . The polymer film thickness is kept constant and equal to h . In the case of very thin films confined between solid plates this will require the application of an external force on the plates. This force need not be explicitly considered in the analysis that follows. The control surface of Fig.5(a) intersects each plate along a plane, at which properties are indistinguishable from those of a bulk s -phase.

Using Eqs.(38) and (76) we can write the total availability of our thermodynamic system as:

$$\begin{aligned}
\underline{r}(T, P_b, n, n_s, a, h; n_f, V_b) &= \underline{r}_f(T, P_b, n_f, a, h) + \underline{r}_b(T, P_b, n - n_f, V_b) + \\
&+ \underline{r}_s(T, P_b, n_s, a) = \\
&= n_f kT \left[\left\{ (r-1)(1 - \ln z) + [-\xi + (r-1) \ln L] \right\} + \frac{L}{n_f} \left\{ 2 \sum_{i=1}^m \left[x \varphi_i \langle \varphi_i \rangle + \ln(1 - \varphi_i) \right] + \right. \right. \\
&\quad \left. \left. + 2m \left(\frac{P_b v^*}{RT} \right) \right\} \right] + \\
&+ (n - n_f) kT \left[(r-1)(1 - \ln z) - \ln r - r x \varphi_b + \frac{r(1 - \varphi_b)}{\varphi_b} \ln(1 - \varphi_b) + \ln \varphi_b + \right. \\
&\quad \left. \frac{P_b v^*}{RT} \frac{r}{\varphi_b} - (r-2) \ln [\lambda_1 + \lambda_0 \tau_L + \lambda_1 \tau_V] \right] + \underline{r}_s(T, P_b, n_s, a)
\end{aligned} \tag{78}$$

The availability of phase s will be assumed to be completely unaffected by the presence of polymer on its surface (incompressible solid or highly attenuated gas; see Assumption 1).

As chosen, our thermodynamic system is a multiphase, multicomponent system, in which the total quantities of all components present are constant, and which is capable of interacting with a constant temperature and constant pressure reservoir. At equilibrium, the total availability $\underline{r}$ of this system must be at a minimum¹⁷ with respect to:

- (a) The amount of polymer between the plates, n_f .
- (b) The volume of the bulk polymer, V_b , or, equivalently, the volume fraction of polymer in the bulk polymer phase.

Then,

$$\left. \frac{\partial \underline{r}}{\partial n_f} \right|_{T, P_b, n, n_s, \underline{a}, h, \underline{V}_b} = 0 \quad (79)$$

$$\left. \frac{\partial \underline{r}}{\partial \varphi_b} \right|_{T, P_b, n, n_s, \underline{a}, h, n_f} = 0 \quad (80)$$

An expression for $\underline{r}$ is provided by Eq.(78). It is convenient to cast this expression in terms of the availability per polymer chain in phases f and b. As mentioned in section II.B, the quantity $-\xi+(r-1)\ln L$ is intensive. It can only depend on n_f through the intensive ratio $\frac{n_f}{\underline{a}}$, or $\frac{n_f}{L}$ (interfacial polymer per unit area). Therefore, Eq.(78) is of the form:

$$\begin{aligned} \underline{r}(T, P_b, n, n_s, \underline{a}, h; n_f, \underline{V}_b) &= n_f \underline{r}_f\left(T, P_b, \frac{n_f}{\underline{a}}, h\right) + (n - n_f) \underline{r}_b(T, P_b, \varphi_b) + \\ &+ \underline{r}_s(T, n_s, \underline{a}) \end{aligned} \quad (81)$$

Then,

$$\begin{aligned} \left. \frac{\partial \underline{r}}{\partial n_f} \right|_{T, P_b, n, n_s, \underline{a}, h, \underline{V}_b} &= \underline{r}_f\left(T, P_b, \frac{n_f}{\underline{a}}, h\right) + n_f \left. \frac{\partial}{\partial n_f} \underline{r}_f\left(T, P_b, \frac{n_f}{\underline{a}}, h\right) \right|_{T, P_b, \underline{a}, h} - \\ &- \underline{r}_b(T, P_b, \varphi_b) = \\ &= \underline{r}_f\left(T, P_b, \frac{n_f}{\underline{a}}, h\right) - \underline{r}_b(T, P_b, \varphi_b) + \frac{n_f}{\underline{a}} \left\{ \frac{\partial}{\partial \left(\frac{n_f}{\underline{a}}\right)} \underline{r}_f\left(T, P_b, \frac{n_f}{\underline{a}}, h\right) \right\}_{T, P_b, h} = \\ &= \underline{r}_f\left(T, P_b, \frac{n_f}{\underline{a}}, h\right) - \underline{r}_b(T, P_b, \varphi_b) - \frac{n_f}{\underline{a}} \frac{1}{\left(\frac{n_f}{\underline{a}}\right)^2} \left\{ \frac{\partial}{\partial \underline{a}} \underline{r}_f\left(T, P_b, \frac{n_f}{\underline{a}}, h\right) \right\}_{T, P_b, n_f, h} = \\ &= \frac{1}{n_f} \underline{r}_f(T, P_b, n_f, \underline{a}, h) - \frac{1}{n - n_f} \underline{r}_b(T, P_b, n - n_f, \underline{V}_b) - \frac{\underline{a}}{n_f} \left\{ \frac{\partial \underline{r}_f(T, P_b, n_f, \underline{a}, h)}{\partial \underline{a}} \right\}_{T, P_b, n_f, h} \end{aligned} \quad (82)$$

From Eqs.(79) and (82) we obtain the equilibrium requirement:

$$\left. \frac{\partial r_f(T, P_b, n_f, a, h)}{\partial a} \right|_{T, P_b, n_f, h} = \frac{1}{a} \left[r_f(T, P_b, n_f, a, h) - \frac{n_f}{n - n_f} r_b(T, P_b, n - n_f, \frac{V_f}{n_f}) \right]$$

or, in simpler notation,

$$a \left. \frac{\partial r_f}{\partial a} \right|_{T, P_b, n_f, h} = n_f [r_f - r_b] \quad (83)$$

On the other hand, Eq.(81) gives:

$$\left. \frac{\partial r}{\partial \phi_b} \right|_{T, P_b, n, n_s, a, h, n_f} = (n - n_f) \left. \frac{\partial r_b(T, P_b, \phi_b)}{\partial \phi_b} \right|_{T, P_b} \quad (84)$$

Combining Eqs.(80) and (84) we obtain:

$$\left. \frac{\partial r_b(T, P_b, \phi_b)}{\partial \phi_b} \right|_{T, P_b} = 0 \quad (85)$$

Eq.(85) expresses the fact that, at full equilibrium, if edge effects are neglected, density in the bulk polymer phase is completely unaffected by the presence of the interfacial polymer. It is equivalent to the optimization requirement, Eq.(67).

In view of Eq.(76) condition (85) becomes:

$$\frac{P_b^v}{RT} + \left(1 - \frac{1}{r}\right) \phi_b + \ln(1 - \phi_b) + x \phi_b^2 = 0 \quad (86)$$

Eq.(86) permits determining ϕ_b , hence V_b , given T and P_b . It is none else than the Sanchez-Lacombe equation of state. Note that conformational energies do not appear in Eq.(86). Our use of the random coil hypothesis in the bulk implies that volumetric behavior will be unaffected by chain stiffness.

In their original work, Sanchez and Lacombe report their equation of state in somewhat different notation; their form can readily be

proved equivalent to Eq.(86). An advantage of Eq.(86) is that it points immediately to the close connection existing between the Sanchez-Lacombe theory of polymer melts and Flory-Huggins thermodynamics of polymer solutions. In the latter⁹, the quantity $\left(1-\frac{1}{r}\right) \phi_b + \ln(1-\phi_b) + \chi \phi_b^2$ is equal to the chemical potential of the solvent in an incompressible solvent/polymer mixture. In the compressible formulation of Sanchez and Lacombe the role of solvent molecules is played by voids, and the quantity

$$\mu^o(T, P_b, \phi_b) = \left(1-\frac{1}{r}\right) \phi_b + \ln(1-\phi_b) + \chi \phi_b^2 + \frac{P_b^v}{RT} \quad (87)$$

is essentially a chemical potential for the voids, relative to a pure "void" phase. The Sanchez-Lacombe equation of state, Eq.(86), is equivalent to the statement that, in the chain/void system representing the bulk polymer, the chemical potential of voids is everywhere equal to zero. The applicability of Flory's ideas on solution thermodynamics to the study of macromolecular liquids was pointed out very early by Kurata and Isida²⁰. They present what is perhaps the earliest derivation of Eq.(68), based on the Flory expression for the Helmholtz energy, in the context of correlating critical constants and boiling points of normal paraffins with chain length.

We now return to the condition of optimization with respect to the amount of interfacial polymer, which we rewrote as Eq.(83). This is equivalent to a maximization of the summand of Eq.(21) with respect to the number of surface sites, L . The derivative

$\left. \frac{\partial \gamma_f}{\partial a} \right|_{T, P_b, n_f, h}$ we have calculated in Eq.(39). Substituting

its value, as well as the values of γ_f and γ_b from Eq.(78) into

Eq.(83), and using Eq.(32) to express n_f , we obtain:

$$\begin{aligned}
 & \frac{La^*}{N_L} 2 \frac{N_L kT}{a^*} \left\{ \left(1 - \frac{1}{r}\right) \sum_{i=1}^m \varphi_i + \sum_{i=1}^m \left[x \varphi_i \langle \varphi_i \rangle + \ln(1 - \varphi_i) \right] + m \left(\frac{P_b v^*}{RT} \right) \right\} = \\
 & = \frac{L}{r} 2 \left[\sum_{i=1}^m \varphi_i \right] kT \left\{ \left[(r-1)(1 - \ln z) + [-\xi + (r-1) \ln L] + \frac{r}{m} 2 \left\{ \sum_{i=1}^m \left[x \varphi_i \langle \varphi_i \rangle + \ln(1 - \varphi_i) \right] + m \left(\frac{P_b v^*}{RT} \right) \right\} \right] \right. \\
 & \quad \left. - \left[(r-1)(1 - \ln z) - \ln r - r x \varphi_b + \frac{r(1 - \varphi_b)}{\varphi_b} \ln(1 - \varphi_b) + \ln \varphi_b + \left(\frac{P_b v^*}{RT} \right) \frac{r}{\varphi_b} - \right. \right. \\
 & \quad \left. \left. -(r-2) \ln(\lambda_1 + \lambda_0 \tau_L + \lambda_1 \tau_V) \right] \right\}
 \end{aligned}$$

or

$$\begin{aligned}
 -\xi + (r-1) \ln L &= \frac{r}{\varphi_b} \left[\left(\frac{P_b v^*}{RT} \right) + \left(1 - \frac{1}{r}\right) \varphi_b + \ln(1 - \varphi_b) + x \varphi_b^2 \right] - 2r x \varphi_b - r \ln(1 - \varphi_b) \\
 &+ \ln \left(\frac{\varphi_b}{r} \right) - (r-2) \ln(\lambda_1 + \lambda_0 \tau_L + \lambda_1 \tau_V)
 \end{aligned} \tag{88}$$

In view of the equation of state (86), Eq.(88) simplifies to:

$$-\xi + (r-1) \ln L = \ln \left(\frac{\varphi_b}{r} \right) - 2r x \varphi_b - r \ln(1 - \varphi_b) - (r-2) \ln(\lambda_1 + \lambda_0 \tau_L + \lambda_1 \tau_V) \tag{89}$$

Eqs.(86) and (89) provide closure to our full equilibrium model.

For a given temperature T and pressure P_b in the bulk phase, the volume fraction φ_b can be determined by solving Eq.(86) for φ_b .

The coefficient $-\xi + (r-1) \ln L$ is then immediately calculable from

Eq.(89). Knowing the value of this coefficient, we can obtain the

entire volume fraction profile in the interfacial region, $\{\varphi_i\}$.

by solving the system of algebraic Eqs. (52), (53), (54), (60) and (61). The molar availabilities in the interfacial and in the bulk region are fixed through Eqs. (38) and (76). Knowing $-\xi + (r-1)\ln L$ and $\{\phi_i\}$ suffices for obtaining all structural and thermodynamic quantities of interest (see Section IV).

B. Formulation of the Problem in Terms of Reduced Free and End Segment Probabilities

Our formulation of the full equilibrium problem is now complete. To emphasize analogies between this and previous interfacial models we introduce a slightly different notation, which invokes "reduced free and end segment probabilities".

We define the quantity P_* as the value assumed by the free segment probability P_i in the limit where the volume fraction ϕ_i becomes equal to the bulk polymer volume fraction at T and P_b [compare Eq. (35)]:

$$\ln P_* = \ln(1 - \phi_b) + 2\phi_b \quad (90)$$

The "reduced free segment probability" p_i in layer i is defined as the ratio

$$p_i = \frac{P_i}{P_*} \quad (91)$$

Let

$$\tau^* = \lambda_1 + \lambda_0 \tau_L + \lambda_1 \tau_V \quad (92)$$

We define the "reduced end segment probability" for a subchain s segments long in layer i by:

$$p(i,s) = \begin{cases} \frac{P(i,s)}{P_*^s} & s=1 \\ \frac{P(i,s)}{P_*^s (\tau^*)^{s-2}} & 2 \leq s \leq r \end{cases} \quad (93)$$

It should be emphasized that neither p_i nor $p(i,s)$ are strictly "probabilities". They can well exceed⁸ the value of 1; they become equal to 1 in the limit $m \rightarrow \infty$, $i \rightarrow \infty$.

In place of the coefficient $-\xi + (r-1)\ln L$ we introduce the quantity:

$$D = \frac{\exp[-\xi + (r-1)\ln L]}{\left(\frac{\phi_b}{r}\right)} P_*^r (\tau^*)^{r-2} \quad (94)$$

The self-consistent set of propagation and segment balance Eqs. (52) to (54), (60) and (61) can now be cast exclusively in terms of $\{\phi_i\}$, D and the lower case p 's. Model equations in the reduced notation are collected in Appendix C.

The distribution of conformations in the interfacial region can be obtained from Eq. (36) as:

$$n_c = LD \left(\frac{\phi_b}{r}\right) \frac{1}{P_*^r (\tau^*)^{r-2}} \left\{ \omega_c \exp\left[-\frac{\epsilon_c}{kT}\right] \right\} \prod_{s=1}^r P_{k(s,c)}$$

or

$$\frac{n_c}{n_f} = D \left[\frac{\frac{m\phi_b}{m}}{\sum_{i=1}^r \phi_i} \right] \left\{ \frac{\omega_c}{2m} \exp\left[-\frac{\epsilon_c - \epsilon}{kT}\right] \right\} \prod_{s=1}^r P_{k(s,c)} \quad (95)$$

where $\bar{\epsilon}_c$, defined by

$$\frac{\bar{\epsilon}_c}{kT} = -(r-2) kT \ln r^* = -(r-2) kT \ln \left\{ \lambda_1 + \lambda_0 \exp\left(-\frac{\epsilon_L}{kT}\right) + \lambda_1 \exp\left(-\frac{\epsilon_V}{kT}\right) \right\} \quad (96)$$

is a conformational free energy per chain in the bulk. In the limit $m \rightarrow \infty$ and full equilibrium between interfacial and bulk polymer Eq.(95) gives a distribution governed completely by intramolecular factors (compare with results in Ref.8).

$$\lim_{m \rightarrow \infty} \frac{n_c}{n_f} = \frac{\omega_c}{2m} \exp\left(-\frac{\bar{\epsilon}_c - \epsilon_c}{kT}\right) \quad (97)$$

The availability per chain in the interfacial region, referred to the bulk [Eqs.(78), (86), (32), (90), (94)] can be written as:

$$\begin{aligned} \frac{1}{kT} \left[\tau_f(T, P_b, h) - \tau_b(T, P_b) \right] &= \frac{r}{m} \left\{ m \left(\frac{P_b^v}{RT} \right)^* + \sum_{i=1}^m \left[\left(1 - \frac{1}{r} \right) \varphi_i + \ln \left(1 - \varphi_i \right) + x \varphi_i \langle \varphi_i \rangle \right] \right\} + \\ &\quad + \ln D \end{aligned} \quad (98)$$

In Eq.(98) we have omitted the intensive quantities $\frac{n_f}{a}$ and φ_b from the arguments of τ_f and τ_b , respectively. This is because $\frac{n_f}{a}$ and φ_b can be obtained from the intensive variables T, P_b and h through the conditions of equilibrium. In Eq.(98) τ_f and τ_b are true "thermodynamic" functions, dependent only on macroscopic variables, and not on microscopic degrees of freedom.

The formulation of Appendix C, as well as the conformation distribution Eq.(95) and the availability Eq.(98) are applicable to

any equilibrium model that provides a value for D . The results of our thermodynamic analysis at full equilibrium can be summarized in the simple statement [Eq.(89),(94)]:

$$D=1 \quad (\text{full equilibrium}) \quad (99)$$

An alternative thermodynamic model, which addresses the case of very small film thicknesses h , and leads to a different value of D , will be introduced in Section IV.

In the case of freely jointed chains ($r_L = r_V = 0$) the full equilibrium model is considerably simplified. The factors $\eta^+(i,s)$, $\eta^0(i,s)$, $\eta^-(i,s)$ and $y(i,s)$, appearing in Eqs.(C.3) and (C.6), all become equal to 1. The formulation outlined in Appendix C becomes essentially identical to the incompressible solution model of Scheutjens and Fleer¹, with voids playing the role of solvent molecules, and with the bulk volume fraction determined by the equation of state (86). In this case our interfacial model bears the same relation to the Scheutjens and Fleer model as the bulk polymer model of Sanchez and Lacombe to Flory-Huggins solution theory. The derivation of Scheutjens and Fleer¹ focuses mainly on conformation propagation and segment balance equations. The condition for closure, Eq.(99), is introduced without justification. The rigorous thermodynamic analysis presented here, based on minimizing the total system availability, makes all assumptions involved evident, and is useful in establishing connections between this lattice model and more general approaches to the surface properties of fluids.

C. Surface Tension and Adhesion Tension

With reference to the thermodynamic system depicted in Fig.5(a) we define interfacial tension γ in terms of the difference between the total availability of phases s, f and b and the availability that the same amount of matter contained in the system would possess, if it belonged entirely to bulk s- and polymer phases under the ambient conditions T and P_b :

$$\begin{aligned}
 2 \gamma a &= n_f \tau_f(T, P_b, h) + n_b \tau_b(T, P_b) + n_s \tau_s(T, P_b, \delta_s) - \\
 &\quad - n_f \tau_b(T, P_b) - n_b \tau_b(T, P_b) - n_s \tau_{sb}(T, P_b) = \\
 &= n_f [\tau_f(T, P_b, h) - \tau_b(T, P_b)] + n_s [\tau_s(T, P_b, \delta_s) - \tau_{sb}(T, P_b)]
 \end{aligned}
 \tag{100}$$

The factor of 2 in Eq.(100) accounts for the presence of two f/s interfaces. The subscript sb denotes a bulk s- phase of infinite extent in all three dimensions; δ_s is the thickness of each s-slab included in the control volume of Fig.5(a). This thickness has been assumed large enough, so that the properties at all points of intersection between the s-phase and the control surface are indistinguishable from those of bulk s. Note that the symbols τ_b and τ_{sb} in Eq.(100) can be substituted by G_b and G_{sb} , respectively; there is no distinction between Gibbs energy and availability in an unconstrained bulk phase.

Consider now the system depicted in Fig.5(a), with all polymer in phases f and b replaced by vacuum. The s-phase remains unaffected by the presence or absence of polymer on its surface, and its

thermodynamic properties are pressure-independent (Assumption 1).

Therefore, in this new, vacuum-filled system it will have exactly the same surface area a and the same molar availability γ_s as in the original system. By definition, then, the difference $\gamma_s(T, P_b, \delta_s) - \gamma_{sb}(T, P_b)$ is related to the surface tension of pure s (against vacuum) by:

$$2 \gamma_s a = n_s [\gamma_s(T, P_b, \delta_s) - \gamma_{sb}(T, P_b)] \quad (101)$$

Combining Eqs.(100) and (101) we obtain:

$$2 (\gamma - \gamma_s) a = n_f [\gamma_f(T, P_b, h) - \gamma_b(T, P_b)] \quad (102)$$

In solid/fluid systems the quantity $-(\gamma - \gamma_s)$ is sometimes referred to as the "adhesion tension"²¹. If the s -phase is a solid, therefore, Eq.(102) provides a route for obtaining the adhesion tension from fundamental molecular information. If the surface tension of the pure solid is known, the interfacial tension γ can also be evaluated. If the s - phase is a gas, then $\gamma_s=0$, and γ on the left hand side of Eq.(102) becomes the surface tension of the pure polymer. No distinction is made here between polymer surfaces exposed to gases and polymer surfaces exposed to vacuum. This is a satisfactory approximation at low pressures, where the thermodynamics of a free polymer surface will be dominated by cohesive energy density and chain conformational statistics. In Appendix D we show that our definition of the adhesion tension in terms of availability, Eq.(102), is consistent with definitions used in previous theoretical work^{16,22}.

Combining Eqs.(102), (32) and (98) we obtain the following simple

expression for the adhesion (resp. surface) tension at a polymer/solid interface (resp. free polymer surface) in terms of the volume fraction profile $\{\phi_i\}$ and the coefficient D:

$$\gamma - \gamma_s = \frac{1}{2 \left(\frac{a}{N_L} \right)^*} \frac{n_f}{L} \left[\tau_f(T, P_b, h) - \tau_b(T, P_b) \right]$$

or

$$\gamma - \gamma_s = \frac{RT}{a^*} \left\{ m \left(\frac{P_b v^*}{RT} \right) + \sum_{i=1}^m \left[\left(1 - \frac{1}{r} \right) \phi_i + \ln(1 - \phi_i) + x \phi_i \langle \phi_i \rangle \right] + \frac{1}{r} \left[\sum_{i=1}^m \phi_i \right] \ln D \right\} \quad (103)$$

It is possible, using Eq.(C.1), to cast Eq.(103) in the equivalent form:

$$\begin{aligned} \gamma - \gamma_s = \frac{RT}{a^*} \left\{ x \sum_{i=1}^m \phi_i \left(\phi_b - \langle \phi_i \rangle \right) - \phi_1 \left(x_s + \lambda_1 x \right) + \right. \\ \left[\sum_{i=1}^m \left(1 - \phi_i \right) \ln(1 - \phi_i) - \left(\sum_{i=1}^m \phi_i \right) \frac{1 - \phi_b}{\phi_b} \ln(1 - \phi_b) \right] + \\ \left. + \left(\frac{P_b v^*}{RT} \right) \left[m - \frac{1}{\phi_b} \left(\sum_{i=1}^m \phi_i \right) \right] + \sum_{i=1}^m \phi_i \ln p_i + \frac{1}{r} \left[\sum_{i=1}^m \phi_i \right] \ln D \right\} \quad (104) \end{aligned}$$

Eq.(104), applied in the limit $\phi_i = \phi_b$ in all layers (constant density model) at full equilibrium, would give:

$$\frac{(\gamma - \gamma_s) a^*}{\phi_b kT} = -\chi_s + \sum_{i=1}^m \ln p_i \quad \left\{ \phi_i = \phi_b, 1 \leq i \leq m \right\} \quad (105)$$

Indeed, Eq.(105) has been derived in the context of a simple, full occupancy model of bulk polymers at interfaces⁸, which assumed $\phi_i = \phi_b = 1$.

More interesting than Eq.(104), and simpler to use, is Eq.(103) for the adhesion tension. Consider the model system of Fig.5(a) with s=gas phase, as the number of layers $m \rightarrow \infty$, so that the middle region of phase f is indistinguishable from phase b. Assuming full equilibrium between bulk and interfacial regions, we can write the polymer surface tension as:

$$\gamma = \frac{RT}{a^*} \sum_{i=1}^m \left\{ \left(\frac{P_{b,i}^v}{RT} \right)^* - \left[-\left(1 - \frac{1}{r}\right) \phi_i - \ln[1 - \phi_i] - \chi \phi_i \langle \phi_i \rangle \right] \right\} \quad (106)$$

The term in the angular brackets of Eq.(106) is very reminiscent of the left-hand side of Eq.(86). Indeed, if we accept that the Sanchez-Lacombe equation of state is followed locally within the interfacial region, then, by applying Eq.(86) to layer i we can write:

$$\left(\frac{P_{T,i}^v}{RT} \right)^* = -\left(1 - \frac{1}{r}\right) \phi_i - \ln[1 - \phi_i] - \chi \phi_i \langle \phi_i \rangle \quad (107)$$

In Eq.(107) the quantity $P_{T,i}$ is the component of pressure in the tangential (x- or y-) direction; in this direction the density of the system is "smeared", and volume fluctuations are not constrained by the layerwise discretization of the lattice.

Combining Eqs.(106) and (107),

$$\gamma = \frac{RT}{a^*} \sum_{i=1}^m (P_b - P_{T,i}) \frac{v^*}{RT} = \sum_{i=1}^m (P_b - P_{T,i}) \ell^* \quad (108)$$

Taking Eq.(108) to the continuum limit $\ell^* \rightarrow \infty$, we rewrite it as:

$$\gamma = \int_{-\infty}^{\infty} [P_b - P_T(z)] dz \quad (109)$$

where the limit $+\infty$ corresponds to the unconstrained bulk polymer and the limit $-\infty$ to the bulk gas phase, in which no polymer is present.

Eq.(109) constitutes^{14,16,23} the "mechanical definition" of γ .

We have shown that our equation (106) is entirely consistent with the mechanical definition of surface tension, if we accept that our interfacial polymer follows locally the equation of state obeyed by the unconstrained bulk. This result points to the internal consistency of our variable density lattice approach, and of our definition of the surface and adhesion tensions.

IV. THERMODYNAMIC ANALYSIS: RESTRICTED EQUILIBRIUM

In the thermodynamic analysis of Section III it was assumed that the interfacial phase f is fully equilibrated with the bulk polymer phase b. In reality this equilibration takes place through diffusion of chains between phases f and b, and is expected to be slow. In a solid/polymer/solid system, at small plate separations (h comparable to chain dimensions) and high molecular weights, the long-range mobility of chains is severely hindered. Full equilibration upon

changing h may never be achieved over the time scale of an experimental measurement.

To deal with this situation, we develop here an alternative thermodynamic approach for solid/polymer/solid systems, which we will refer to as the "restricted equilibrium model". In this approach the interfacial polymer f is equilibrated with the bulk polymer b with respect to temperature and pressure distribution, but not with respect to mass exchange. Polymer chains in the central region between the plates do not "feel" the presence of polymer chains in the bulk, other than through the temperature and pressure of the bulk phase. This is because, over the time scale of interest, chains from the bulk do not have the chance to migrate into the interfacial region, and vice versa. In other words, the mechanism, whereby chemical potential equalization would occur between phases f and b , is hindered. Upon introducing a change in the macroscopic constraints of the system (e.g. changing the plate separation), the interfacial chains rearrange themselves locally, optimizing their density and conformation with respect to their immediate surroundings in the interfacial region. No global equilibration with respect to the bulk occurs, however, as chains in the interfacial region do not have a full appreciation of how chains in the bulk look like.

Mathematically, the restricted equilibrium approach treats the interfacial polymer as an infinite film between two smooth solid surfaces, at equilibrium with a work (pressure P_b) and heat (temperature T) but not mass (chemical potential) reservoir. We pick our thermodynamic system as pictured in Fig.5(b). It consists

of a constant amount of polymer, containing n_f chains, between two solid plates at separation h . The surface area $\underline{a}$, that the system occupies on each plate, is a variable to be determined from the condition of equilibrium. The interfacial polymer system we are focusing on is surrounded by similar systems on all sides not bounded by solid. The bulk polymer does not enter our thermodynamic analysis, other than through its temperature and pressure.

We have picked a system of constant mass, capable of interacting with a constant temperature and pressure reservoir. At thermodynamic equilibrium¹⁷ the availability of our system must be at a minimum:

$$\underline{\gamma} \left(T, P_b, n_f, \underline{a}, h \right) = \underline{\gamma}_f \left(T, P_b, n_f, \underline{a}, h \right) = \min \quad (110)$$

with respect to the surface area $\underline{a}$.

The function $\underline{\gamma}_f$ is given by Eq.(38). Note that the statistical mechanical analysis that led to this equation assumes internal equilibration among of all conformations within the interfacial among all chains in phase f have the same chemical potential, but this is not necessarily the chemical potential of a bulk polymer phase at T and P_b .

The minimization, Eq.(110), implies:

$$\left. \frac{\partial \underline{\gamma}_f}{\partial \underline{a}} \right|_{T, P_b, n_f, h} = 0 \quad (111)$$

The derivative appearing in Eq.(111) has been expressed in terms of microscopic degrees of freedom in Eq.(39). Using that expression here, we obtain:

$$\left(\frac{P_b v^*}{RT}\right) + \frac{1}{m} \sum_{i=1}^m \left\{ \left(1 - \frac{1}{r}\right) \phi_i + \ln(1 - \phi_i) + \chi \phi_i \langle \phi_i \rangle \right\} = 0 \quad (112)$$

Eq.(112) provides closure to our interfacial model in the restricted equilibrium case. The system of equations to be solved consists of the free segment probability definition, Eq.(35), the recursive conformation propagation equations (52), (53) and (54), the segment balance equations (60) and (61), and Eq.(112). It can be regarded as a system of $(m+1)$ equations [Eqs.(61) and (112)] in $(m+1)$ unknowns: the volume fractions $\{\phi_i\}$ ($1 \leq i \leq m$) and the coefficient $-\xi + (r-1)\ln L$; all other equations are essentially definitions, to be used with Eqs.(61). A reduced probability notation is introduced as in the full equilibrium case (Appendix C). Note that here this is done merely for convenience. The volume fraction ϕ_b is not involved in the physics of the restricted equilibrium problem. In reduced notation the restricted equilibrium model is contained in Eqs.(36), (C.1) to (C.7), and (112). It can be regarded as a system of $(m+1)$ equations in the $(m+1)$ unknowns $\{\phi_i\}$ ($1 \leq i \leq m$) and D . Unlike what happens in the full equilibrium case, the value of D is not given by a trivial expression, such as Eq.(99); it has to be obtained from the solution of the interfacial model.

Eq.(112) bears a remarkable resemblance to the Sanchez-Lacombe Eq.(86). Although the volume fraction profile $\{\phi_i\}$ is nonuniform, the restricted equilibrium with a reservoir at T and P_b leads to an equation-of-state-like relationship, obeyed by the film as a whole.

The restricted equilibrium model will be used for exploring some

intriguing aspects of the interfacial behavior of polymer melts, confined between closely spaced surfaces.

V. STRUCTURAL FEATURES

The molecular detail built into our lattice model allows us to obtain a variety of interesting structural features from the model solution $\{\phi_i, D\}$. Techniques for calculating some of these features have been developed in Ref.8, in the context of a simpler, constant density model for polymer and copolymer melts at interfaces. Here we extend these techniques, to take into account density variations and conformational energy effects. The presentation is brief; a more complete treatment of the fundamentals is available in Ref.8. The expressions developed here are applicable to both the full equilibrium and the restricted equilibrium models.

A. Bond Orientation

In our cubic lattice, let n_{bi}^L be the total number of bonds per surface site that lie parallel to the s/f interface in layer i. Let also n_{bi}^N be the number of bonds per surface site that connect layers i and (i+1), and are therefore directed perpendicular to the interface. We can consider bond s of a chain as joining two subchains, of lengths s and (r-s) (Fig.6). The probability that bond s lies flat in layer i is proportional to the quantity:

$$\lambda_0 p(i,s) p(i,r-s) \frac{1}{\tau^*} \left\{ \frac{\lambda_1 \tau_L p(i-1,r-s-1) + \left[(\lambda_0 - 2\lambda_1) \tau_L + \lambda_1 \tau_V + \lambda_1 \right] p(i,r-s-1) + \lambda_1 \tau_L p(i+1,r-s-1)}{\lambda_1 p(i-1,r-s-1) + \lambda_0 p(i,r-s-1) + \lambda_1 p(i+1,r-s-1)} \right\}$$

if s=1

$$\lambda_0 p(i,s) p(i,r-s) \frac{1}{\left(\tau^*\right)^2} \left\{ \frac{\lambda_1 \tau_L p(i-1, r-s-1) + \left[(\lambda_0 - 2\lambda_1) \tau_L + \lambda_1 \tau_V + \lambda_1 \right] p(i, r-s-1) + \lambda_1 \tau_L p(i+1, r-s-1)}{\lambda_1 p(i-1, r-s-1) + \lambda_0 p(i, r-s-1) + \lambda_1 p(i+1, r-s-1)} \right\}$$

$$\left\{ \frac{\lambda_1 \tau_L p(i-1, s-1) + \left[(\lambda_0 - 2\lambda_1) \tau_L + \lambda_1 \tau_V + \lambda_1 \right] p(i, s-1) + \lambda_1 \tau_L p(i+1, s-1)}{\lambda_1 p(i-1, s-1) + \lambda_0 p(i, s-1) + \lambda_1 p(i+1, s-1)} \right\}$$

if $2 \leq s \leq r-2$

$$\lambda_0 p(i,s) p(i,r-s) \frac{1}{\tau^*} \left\{ \frac{\lambda_1 \tau_L p(i-1, s-1) + \left[(\lambda_0 - 2\lambda_1) \tau_L + \lambda_1 \tau_V + \lambda_1 \right] p(i, s-1) + \lambda_1 \tau_L p(i+1, s-1)}{\lambda_1 p(i-1, s-1) + \lambda_0 p(i, s-1) + \lambda_1 p(i+1, s-1)} \right\}$$

if $s = r-1$

Introducing the notation of Appendix C [Eq. (C.4)], the above expressions can be summarized as:

$$\lambda_0 p(i,s) p(i,r-s) \eta^0(i,s+1) \eta^0(i,r-s+1) \quad (113)$$

Expression (113) stems directly from the product form of the conformation distribution in our lattice model [Eq. (40)]. The conformation-dependent η^0 factors incorporate the intramolecular energy contributions due to the bond pairs $(s-1,s)$ and $(s,s+1)$, which are not included in the end segment probabilities $p(i,s)$ and $p(i,r-s)$. A preaveraging approximation has been used, exactly as in the derivation of Eqs. (52) and (61).

Similarly, the probability that bond s connect layers i and $(i+1)$, with segment s in layer i and segment $(s+1)$ in layer $(i+1)$, is proportional to the quantity:

$$\lambda_1 p(i,s) p(i+1,r-s) \eta^+(i+1,s+1) \eta^-(i,r-s+1) \quad (114)$$

and the probability that bond s connect layers i and $(i+1)$, with segment s in layer $(i+1)$ and segment $(s+1)$ in layer i , is proportional to the quantity:

$$\lambda_1 p(i+1,s) p(i,r-s) \eta^-(i,s+1) \eta^+(i+1,r-s+1) \quad (115)$$

There is a total of $\frac{L}{r} \sum_{i=1}^{2m} \phi_i$ bonds of order s in the interfacial polymer. The total number of bonds per surface site, irrespective of order, that lie flat in layer i , will then be:

$$n_{bi}^L = \frac{\lambda_0}{r} \left(\sum_{i=1}^{2m} \phi_i \right) \sum_{s=1}^{r-1} \frac{p(i,s) p(i,r-s) \eta^0(i,s+1) \eta^0(i,r-s+1)}{p_b(s)} \quad (116)$$

and the total number of bonds per surface site, irrespective of order that connect layers i and $(i+1)$, and therefore lie normal to the surface, will be:

$$n_{bi}^N = \frac{\lambda_1}{r} \left(\sum_{i=1}^{2m} \phi_i \right) \sum_{s=1}^{r-1} \frac{p(i,s)p(i+1,r-s)\eta^+(i+1,s+1)\eta^-(i,r-s+1) + p(i+1,s)p(i,r-s)\eta^-(i,s+1)\eta^+(i+1,r-s+1)}{p_b(s)} \quad (117)$$

where

$$\begin{aligned}
 p_b(s) = & \lambda_0 \sum_{i=1}^{2m} p(i,s) p(i,r-s) \eta^0(i,s+1) \eta^0(i,r-s+1) + \\
 & + \lambda_1 \sum_{i=1}^{2m-1} p(i,s) p(i+1,r-s) \eta^+(i+1,s+1) \eta^-(i,r-s+1) \\
 & + \lambda_1 \sum_{i=1}^{2m-1} p(i+1,s) p(i,r-s) \eta^-(i,s+1) \eta^+(i+1,r-s+1)
 \end{aligned} \tag{118}$$

The bond numbers n_{bi}^L and n_{bi}^N obey the obvious normalization:

$$\sum_{i=1}^{2m} n_{bi}^L + \sum_{i=1}^{2m-1} n_{bi}^N = \frac{n_f}{L}(r-1) = \left(\frac{r-1}{r} \right) \left(\sum_{i=1}^{2m} \phi_i \right) \tag{119}$$

We define a bond order parameter⁸ S_i for layer i , as

$$S_i = \frac{1}{2} \left[3 \frac{n_{bi-1}^N + n_{bi}^N}{n_{bi-1}^N + n_{bi}^N + 2n_{bi}^L} - 1 \right] \tag{120}$$

S_i is a sensitive measure of orientation effects induced by the presence of interfaces. It assumes positive (negative) values, if the prevalent orientation of bonds emanating from layer i is perpendicular (resp. parallel) to the surface; a value of $S_i = 0$ will indicate a completely random arrangement of bonds.

In the limit $m \rightarrow \infty$, in a cubic lattice, far away from any surface, the quantities n_i^N , n_i^L , S_i approach the values:

$$\left. \begin{aligned}
 \lim_{i \rightarrow \infty} n_{bi}^N &= \frac{1}{3} \varphi_i \frac{r-1}{r} \\
 \lim_{i \rightarrow \infty} n_{bi}^L &= \frac{2}{3} \varphi_i \frac{r-1}{r} \\
 \lim_{i \rightarrow \infty} S_i &= 0
 \end{aligned} \right\} \quad (121)$$

B. Chain Shape Profiles

To characterize chain shape as a function of position in the interfacial region, we introduce the quantity n_{si} , defined as the average number of segments that a chain passing through layer i occupies in that layer. This quantity can be seen as the average "width" of a chain passing through layer i . The n_{si} profile is calculated as follows:

Let

$$= \begin{bmatrix}
 \lambda_0 \eta^0(1,s)p_1 & \lambda_1 \eta^-(1,s)p_1 & 0 & . & . & . & 0 \\
 \lambda_1 \eta^+(2,s)p_2 & \lambda_0 \eta^0(2,s)p_2 & \lambda_1 \eta^-(2,s)p_2 & . & . & . & . \\
 0 & . & . & . & . & . & . \\
 . & . & \lambda_1 \eta^+(i,s)p_i & \lambda_0 \eta^0(i,s)p_i & \lambda_1 \eta^-(i,s)p_i & . & . \\
 . & . & . & . & . & . & 0 \\
 . & . & . & . & \lambda_1 \eta^+(2m-1,s)p_{2m-1} & \lambda_0 \eta^0(2m-1,s)p_{2m-1} & \lambda_1 \eta^-(2m-1,s)p_{2m-1} \\
 0 & . & . & . & 0 & \lambda_1 \eta^0(2m,s)p_{2m} & \lambda_0 \eta^0(2m,s)p_{2m}
 \end{bmatrix}$$

(122)

be the matrix appearing in the recursive conformation propagation Eqs.(C.3), if those are written for the entire interfacial domain $1 \leq i \leq 2m$.

Let also $w'_{(i)}$ be a modification of matrix w , obtained by substituting $p_i=0$ in it. (This substitution will reduce the entire i^{th} row of matrix $w'_{(i)}$ to zeros; it will also affect rows $(i-2), (i-1), (i+1), (i+2)$, through modifying the η -coefficients in these rows.)

Let $p'_{(i)}$ be the $2m$ -long vector of reduced free segment probabilities, modified by substituting 0 as its i^{th} element:

$$p'_{(i)} = \text{col}(p_1, p_2, \dots, p_{i-1}, 0, p_{i+1}, \dots, p_{2m}) \quad (123)$$

We form a sequence of s vectors, each $2m$ -long, using the definition and recursive scheme:

$$p'_{(i)}(s) = \text{col}[p'_{(i)}(1,s), p'_{(i)}(2,s), \dots, p'_{(i)}(2m,s)] \quad (124)$$

$$p'_{(i)}(s) = w'_{(i)} p'_{(i)}(s-1); \quad p'_{(i)}(1) = p'_{(i)} \quad (125)$$

We define the reduced chain probability for not passing through layer i by

$$p'_{(i)}(r) = \bigvee_{j=1}^{2m} p'_{(i)}(j,r) \quad (126)$$

and the total reduced chain probability by

$$p(r) = \bigvee_{j=1}^{2m} p(j,r) \quad (127)$$

The average chain width in layer i is obtained from:

$$\frac{\varphi_i}{n_{si}} = \frac{1}{r} \left[\bigvee_{i=1}^{2m} \varphi_i \right] \left[1 - \frac{p'_{(i)}(r)}{p(r)} \right] \quad (128)$$

The $\{n_{si}\}$ profile is a useful quantitative measure of conformational perturbations induced by the presence of interfaces.

C. Distribution of Segments of Given Order Within the Interfacial Region

The volume fraction profile $\{\phi_i\}$ provides information on the distribution of mass in the interfacial region. Individual segments along the chains do not necessarily conform to this distribution, however. Chain ends, for example, may exhibit a preference for the surface region, as opposed to the bulk, and thus distribute according to a profile that departs significantly from $\{\phi_i\}$. To explore the spatial distribution of segments as a function of their topological role in the chain backbone, we introduce separate volume fractions for segments of different order. The quantity $\phi_i(s)$ will be used to denote the volume fraction of s-type segments in layer i. The $\phi_i(s)$ profiles obey the symmetry condition,

$$\phi_i(s) = \phi_i(r-s+1) \quad 1 \leq i \leq m, \quad 1 \leq s \leq r \quad (129)$$

and the normalization condition,

$$\phi_i = \sum_{s=1}^r \phi_i(s) \quad 1 \leq i \leq m \quad (130)$$

In place of volume fractions one can use mass densities (in g/cm^3), defined by:

$$\rho_i(s) = \frac{M}{rv^*} \phi_i(s) \quad (131)$$

$$\rho_i = \frac{M}{rv^*} \phi_i \quad (132)$$

The ratio $\frac{\rho_i(s) r}{\rho_i}$ is a direct measure of preferential enhancement/depletion effects exhibited by segments of a given order.

Within the framework of the lattice model presented here, the volume fraction $\phi_i(s)$ can be calculated as:

$$\phi_i(s) = \phi_b \left(\frac{D}{r} \right) \frac{1}{p_i} p(i,s) p(i,r-s+1) y(i,s) \quad (133)$$

$1 \leq i \leq m, 1 \leq s \leq r$

where $y(i,s)$ is defined in Eqs.(C.6).

Eq.(133) gives the contribution to polymer density in layer i from chain segments of order i . The physical meaning of Eq.(133) becomes evident in the light of Eqs.(130) and (C.7).

VI. THE FULL EQUILIBRIUM MODEL IN THE CONTINUUM LIMIT

A continuum (lattice-free) theoretical formulation, known as the "self-consistent field approach", has enjoyed widespread use in the study of interface-related polymer problems. This approach, strictly valid in the limit of infinitely long chains and not too strong interaction energies, is based on Edwards' propagator method for dealing with chain conformations²⁴. The multichain problem is substituted by a partial differential "diffusion-reaction" equation, that provides a probabilistic description of the propagation of single chain conformations. The effects of the presence of other chains, and of the surface, are incorporated within a spatially varying "free energy" field, which appears in the "reaction" term of the differential equation; this field is related to chain conformations through self-consistency requirements. The self-

consistent field approach has been used to study immiscible polymer/polymer interfaces²⁵, the microdomain structure of block copolymers²⁶, the surface of concentrated polymer solutions²⁷, and polymer adsorption from solution on solid surfaces²⁸.

In this section we will explore the relationship between our thermodynamics-based variable density lattice model and self-consistent-field-type approaches. To do this, we will examine our full equilibrium formulation, Eqs.(86), (C.1) to (C.7), (92) and (99), in a continuum limit, where the lattice disappears. Consider the model polymer of Fig.1, exposed to gas or solid phases across plane interfaces perpendicular to the z-direction. For simplicity, assume that chains are freely jointed, i.e. $T_L = T_V = 0$. In this case all η_i 's become equal to 1; the conformation propagation equations (C.3), upon substitution of λ_0 by $1-2\lambda_1$, can be written as:

$$p(i,s) = p(i,1) \left\{ p(i,s-1) + \lambda_1 \left[p(i+1,s-1) + p(i-1,s-1) - 2p(i,s-1) \right] \right\} \quad (134)$$

We change variables from (i,s) to (z,t) . The distance z normal to the surface is discretized in the lattice representation, with a stepsize $\Delta z = \ell^*$. The variable t is a measure of a segment's position along a chain, defined by:

$$t = \frac{s}{r} \quad 0 \leq t \leq 1 \quad (135)$$

and varying in steps of size $\Delta t = 1/r$.

Upon adding and subtracting the term $p(i,1)p(i,s)$ Eq.(134) becomes:

$$\left[1 - p(z, \frac{1}{r}) \right] p(z,t) = -p(z, \frac{1}{r}) \left[\frac{1}{r} \frac{p(z,t) - p(z,t-\Delta t)}{\Delta t} - \lambda_1 (\ell^*)^2 \frac{p(z+\Delta z, t-\Delta t) + p(z-\Delta z, t-\Delta t) - 2p(z, t-\Delta t)}{(\Delta z)^2} \right] \quad (136)$$

If now one assumes that:

- (a) The system is composed of long chains: $r \gg 1$
- (b) Structural variations in the interfacial region occur on a length scale δ_f , that is much larger than monomer size: $b \ll \delta_f$, then one can substitute the finite difference expressions in Eq.(136) by derivatives, taking $\Delta t \rightarrow 0$, $\Delta z \rightarrow 0$:

$$\lambda_1 b^2 \frac{\partial^2 p(z,t)}{\partial z^2} - \frac{1}{r} \frac{\partial p(z,t)}{\partial t} + \left[1 - \frac{1}{p(z, \frac{1}{r})} \right] p(z,t) = 0 \quad (137)$$

Eq.(137) is a diffusion-reaction partial differential equation. In the "diffusivity" term we have substituted ℓ^* by the Kuhn segment length, b . For freely jointed chains, $b = \ell^*$. In the presence of intrachain stiffness the characteristic length for propagation of unperturbed chain conformations is larger than monomer size. In our lattice model this effect is incorporated in the η factors of Eq.(C.3). Eq.(137), which is none else than the Edwards-Helfand diffusion equation, implies that the diffusive nature of conformation propagation, observed for $b = \ell^*$, is preserved in the presence of chain stiffness. The Edwards-Helfand $G(z,s)^{28}$ or $q(x,t)^{26}$ function is the same as the Scheutjens-Fleer "reduced end segment probability", p , expressed in continuum terms.

We now elaborate on the $p(z, \frac{1}{r})$ term appearing in Eq.(137). In a continuum formulation, instead of a discrete volume fraction profile, one uses a continuum volume fraction profile, or, equivalently, a continuum mass density profile, $\rho(z)$. In the bulk, density assumes an asymptotic value, ρ_b , which, at given T and P_b ,

can be found from the Sanchez-Lacombe equation of state, Eq.(86):

$$\frac{P_b}{P^*} + \left(\frac{T}{T^*}\right) \left[\left(1 - \frac{1}{r}\right) \left(\frac{\rho_b}{\rho_b^*}\right) + \ln\left(1 - \frac{\rho_b}{\rho_b^*}\right) \right] + \left(\frac{\rho_b}{\rho_b^*}\right)^2 = 0 \quad (138)$$

where

$$\rho_b^* = \lim_{\substack{P_b \rightarrow \infty \\ \text{or } T \rightarrow 0}} \rho_b(T, P_b) = \frac{M}{rv^*} \quad (139)$$

is the "hard core" density of the polymer, corresponding to a fully occupied lattice.

In the continuum formulation, we describe the interaction between two segments by a separation-dependent potential function. This consists of a hard-sphere repulsive core, at separation $R = \ell^*$, and an attractive tail, $u_{AA}(R)$. Also, the interaction between one of the semiinfinite solid domains and a segment at distance z from its surface is described by a potential function, consisting of a hard-sphere repulsive core at ℓ^* , and an attractive tail, $u_{AS}(z)$. In a lattice representation, the functions u_{AA} and u_{AS} are square wells of width ℓ^* ; more realistically, they can include long-range tails. In the continuum limit, the lattice quantity $-kT \left[x_s + \lambda_1 x \right] \left[\delta_{i1} + \delta_{im} \right]$ is substituted by $u_{AS}(z)$. Also, the lattice quantity $-kT \left[2x \left(\langle \phi_i \rangle - \phi_b \right) \right]$ must be substituted by

$$2\pi \int_{\ell^*}^{h-\ell^*} d\zeta \int_0^\infty R dR \left[\frac{rN_L}{M} \rho(\zeta) \right] u_{AA} \left[\left\{ (z-\zeta)^2 + R^2 \right\}^{1/2} \right] - 4\pi \left[\frac{rN_L}{M} \rho_b \right] \int_{\ell^*}^\infty R^2 u_{AA}(R) dR$$

The first term in the above expression is the total attractive energy experienced by a segment as a result of interactions with other segments in the interfacial region. The second term is the total

attractive energy that this segment would experience in the unconstrained bulk. Note that this expression essentially approximates the pair distribution function of the fluid of segments by a unit step function.

With this treatment of energetics, the free segment probability definitions, Eq.(C.1), assume the continuum form:

$$p(z, \frac{1}{r}) = \exp\left[-\frac{u(z)}{kT}\right] \quad (140)$$

$$u(z) = u_{AS}(z) + 2\pi \left\{ \int_{\ell^*}^{h-\ell^*} d\zeta \int_{\ell^*}^{\infty} R dR \left[\frac{rN_L}{M} \rho(\zeta) \right] u_{AA} \left[\left\{ (z-\zeta)^2 + R^2 \right\}^{1/2} \right] - \right. \\ \left. - 2 \left[\frac{rN_L}{M} \rho_b \right] \int_{\ell^*}^{\infty} R^2 u_{AA}(R) dR \right\} - kT \ln \left[\frac{\rho_b^* - \rho(z)}{\rho_b^* - \rho_b} \right] \quad (141)$$

The energy function $u(z)$ is a "self consistent field". It can loosely be characterized as a chemical potential per segment at position z . Eq.(141) shows clearly the energy and entropy contributions to $u(z)$. The logarithmic form of the latter stems directly from the use of Flory statistics in our variable density model.

Closure of the model requires consideration of the segment balance Eqs.(C.6). For freely jointed chains and full equilibrium, the continuum counterparts of these equations are:

$$\frac{\rho(z)}{\rho_b} p(z, \frac{1}{r}) = \int_{\frac{1}{r}}^1 p(z, t) p(z, 1-t) dt \quad (142)$$

The density profile obeys the boundary conditions:

$$\rho(\ell^*) = \rho(h-\ell^*) = 0 \quad (143)$$

The integrodifferential system of Eqs.(137), (140), (141), (142), together with Eqs.(138), (139) and the boundary conditions (143), constitutes a continuum limit of our variable density lattice model. The similarity with "self-consistent field" approaches^{26,28} is evident.

In particular, if one assumes that

(c) The "self consistent field" is very weak in comparison to kT :

$$\frac{u(z)}{kT} \ll 1$$

then equation (140) gives:

$$\frac{1}{p(z, \frac{1}{r})} = \exp\left[\frac{u(z)}{kT}\right] \approx 1 + \frac{u(z)}{kT}$$

which, upon combining with Eq.(137), gives the diffusion equation:

$$\lambda_1 b^2 \frac{\partial^2 p(z,t)}{\partial z^2} - \frac{1}{r} \frac{\partial p(z,t)}{\partial t} - \frac{u(z)}{kT} p(z,t) = 0 \quad (144)$$

Moreover, putting $p(z, 1/r) \approx 1$ and $1/r \approx 0$ in Eq.(142), one obtains:

$$\rho(z) = \rho_b \int_0^1 p(z, t) p(z, 1-t) dt \quad (145)$$

Eqs.(144) and (145) are exactly the self-consistent field equations used in the Helfand and Tagami theory of polymer-polymer interfaces²⁶. Note that assumption (c) would also imply assumption (b). The above derivation of Eqs.(137) to (142) indicates that continuum, self-consistent field formulations do not possess more physical content

than discrete, Scheutjens and Fleer-type formulations. On the contrary, the continuum approaches commonly used are more restrictive in terms of the approximations they invoke. A merit of the continuum formulation derived here is that it can incorporate long-range segment-segment and segment-surface interactions; also, that it employs a lattice-independent parametric representation. A disadvantage of the continuum formulation is the fact that it relies on assumption (b). As we shall see, density and conformation variations at free melt surfaces and melt/solid interfaces are quite sharp, of a length scale commensurate to the Kuhn segment length. Thus, use of a diffusion equation is not generally justifiable. Despite its artificial discreteness, the original lattice formulation is based on a rigorous statistical mechanical analysis of the multichain system, that retains its applicability in the presence of sharp gradients.

The system of integrodifferential equations (137) to (142), that describe the interfacial problem in the continuum limit, is highly complex. Its analytical solution would necessitate the introduction of further mathematical simplifications (in addition to assumptions (a), (b)), such as those leading to Eqs. (144) and (145), and those that have been employed in all previous self-consistent field calculations. These simplifications sacrifice "exactness" for the sake of mathematical elegance, but thus degrade the predictive power of the continuum model. If, on the other hand, one implemented a numerical finite difference scheme to solve the full continuum problem, one would inevitably revert to a discrete, lattice

representation. In summary, there is not much incentive for preferring a continuum, "self-consistent field"-type formulation to a lattice formulation. On the contrary, the lattice, perhaps with appropriate refinement, so that results are coordination-number insensitive and long-range interactions are taken into account, offers a good combination of rigor, realism and tractability.

VII. CONCLUDING REMARKS

We have introduced a self-consistent, mean field, variable density lattice model for polymer melt surfaces and polymer melt/solid interfaces. This model can predict surface thermodynamic properties (surface tension, adhesion tension), as well as detailed structural features (segment density distribution, bond orientation, chain shape and size characteristics), based only on the Sanchez-Lacombe equation of state parameters.

The model was derived through a coherent statistical mechanical and thermodynamic analysis, that invokes no phenomenological concepts foreign to the lattice representation. The formulation of the interfacial equilibrium problem is completely rigorous, based on the concept of availability. It leads to an expression for surface tension that is consistent with the mechanical definition of surface tension. The set of equations summarizing this model of melts is analogous to the Scheutjens and Fleer model of polymer solutions, with voids playing the role of solvent molecules.

Techniques have been developed for incorporating intramolecular energy effects in the variable density lattice model in a mean field sense. Moreover, a quantitative connection between the lattice model and continuum "self-consistent field" formulations has been established.

In recognition of the severe limitations to chain transport, that may exist in highly confined liquid polymer films, two alternative forms of the variable density model were developed. The first, referred to as the "full equilibrium model", assumes that the polymer in the interfacial region is completely equilibrated with the unconstrained bulk, with respect to temperature, pressure and mass exchange. It is applicable to interfaces formed between polymer phases of macroscopic dimensions, and solids or gases. The second form, termed the "restricted equilibrium model", was developed specifically for polymer films of thickness commensurate with chain dimensions, confined between solid surfaces. It pictures the confined film as a microphase of essentially infinite extent in two directions, that reorganizes itself locally in response to the temperature and pressure of the bulk phase, but cannot freely exchange chains with the bulk.

Results from applying the variable density model to specific melt/gas and melt/solid systems will be reported in subsequent publications.

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18. The notation of Modell and Reid will be followed here. Underbars will denote total (extensive) properties. Symbols without underbars will denote molar or intensive properties. Thus, $\underline{V}$ is a total volume, in m^3 , whereas V is a molar volume, in m^3/mol .
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APPENDIX A: DERIVATION OF EQ.(38) FOR THE AVAILABILITY OF THE INTERFACIAL POLYMER

We present here a detailed derivation of Eq.(38), that gives the availability of the interfacial polymer, from Eqs.(12),(19),(20),(22),(26),(29),(30),(31),(32) and the conformation distribution, Eq.(36).

Substituting Eqs.(19),(20) and (26) in Eq.(22) and using Stirling's approximation for all factorials, we obtain:

$$\begin{aligned}
 \frac{1}{kT} \gamma_f(T, P_b, n_f, a, h) = & -2mL \ln L + 2mL - (r-1) n_f \ln z + (r-1) n_f \ln L + \\
 & + \sum_c n_c \ln \left(\frac{n_c}{\omega_c} \right) - \sum_c n_c + \sum_{i=1}^{2m} n_i^o \ln n_i^o - \sum_{i=1}^{2m} n_i^o - \\
 & - x \sum_{i=1}^{2m} \left\{ \sum_c n_c r_{i,c} \left[\sum_{j=1}^{2m} \left(\lambda_{j-i} \frac{\sum_c n_c r_{j,c}}{L} \right) \right] \right\} - \\
 & - \left(x_s + \lambda_1 x \right) \sum_c n_c \left(r_{1,c} + r_{2m,c} \right) + \sum_c n_c \left(\frac{\epsilon_c}{kT} \right) + 2mL \left(\frac{P_b v^*}{RT} \right)
 \end{aligned}
 \tag{A.1}$$

We now insert the conformation distribution, Eq.(36), in Eq.(A.1) and at the same time use the definitions of volume fractions, Eqs.(29) and (30), and Eqs.(12) and (32), to obtain:

$$\begin{aligned}
\frac{1}{kT} \bar{r}_f(T, P_b, n_f, a, h) &= -2mL \ln L + 2mL - (r-1)n_f \ln z + (r-1)n_f \ln L + \\
&+ \sum_c \sum_{i=1}^{2m} n_c \left[\left(-\xi + r \ln L \right) - \frac{\epsilon_c}{kT} + \sum_{i=1}^{2m} r_{i,c} \ln P_i \right] - n_f + L \ln L \sum_{i=1}^{2m} (1-\varphi_i) + \\
&+ L \sum_{i=1}^{2m} (1-\varphi_i) \ln(1-\varphi_i) - L \sum_{i=1}^{2m} (1-\varphi_i) - xL \sum_{i=1}^{2m} \varphi_i \langle \varphi_i \rangle - \\
&- \left(x_s + \lambda_1 x \right) L \left(\varphi_1 + \varphi_{2m} \right) + \sum_c n_c \left(\frac{\epsilon_c}{kT} \right) + 2mL \left(\frac{P_b v^*}{RT} \right) = \\
&= \ln L \left\{ -2mL + (r-1)n_f + n_f r + 2mL - L \sum_{i=1}^{2m} \varphi_i \right\} + \\
&+ \left\{ 2mL - 2mL - n_f + L \sum_{i=1}^{2m} \varphi_i \right\} - n_f \left\{ (r-1) \ln z + \xi \right\} + \\
&+ \left[\sum_c n_c \left(\frac{\epsilon_c}{kT} \right) - \sum_c n_c \left(\frac{\epsilon_c}{kT} \right) \right] + L \sum_{i=1}^{2m} \varphi_i \ln P_i + L \left\{ x \sum_{i=1}^{2m} \varphi_i \langle \varphi_i \rangle + \sum_{i=1}^{2m} \ln(1-\varphi_i) \right\} - \\
&- L \sum_{i=1}^{2m} \varphi_i \left\{ \ln(1-\varphi_i) + 2x \langle \varphi_i \rangle + \left(\delta_{i1} + \delta_{i2m} \right) \left(x_s + \lambda_1 x \right) \right\} + 2mL \left(\frac{P_b v^*}{RT} \right)
\end{aligned}
\tag{A.2}$$

In view of Eq.(32), Eq.(A.2) immediately simplifies to:

$$\begin{aligned}
 \frac{1}{kT} \underline{r}_f(T, P_b, n_f, \underline{a}, h) &= n_f \left[(r-1) \ln L + (r-1) - (r-1) \ln z - \xi \right] + \\
 &+ L \left\{ x \sum_{i=1}^{2m} \varphi_i \langle \varphi_i \rangle + \sum_{i=1}^{2m} \ln(1-\varphi_i) \right\} + \\
 &+ L \sum_{i=1}^{2m} \varphi_i \left\{ \ln P_i - \ln(1-\varphi_i) - 2x \langle \varphi_i \rangle - [\delta_{i1} + \delta_{i2m}] [x_s + \lambda_1 x] \right\} + 2mL \left(\frac{P_b^v}{RT} \right)
 \end{aligned}
 \tag{A.3}$$

Using the definition, Eq.(35), and taking into account the symmetry wrt. the midplane between layers m and $m+1$, we immediately obtain:

$$\begin{aligned}
 \frac{1}{kT} \underline{r}_f(T, P_b, n_f, \underline{a}, h) &= n_f \left[(r-1) \{1 - \ln z + \ln L\} - \xi \right] + \\
 &+ 2L \sum_{i=1}^m \left\{ x \varphi_i \langle \varphi_i \rangle + \ln(1-\varphi_i) \right\} + 2mL \left(\frac{P_b^v}{RT} \right)
 \end{aligned}$$

which is Eq.(38), Q.E.D.

APPENDIX B: CALCULATION OF THE DERIVATIVE OF THE AVAILABILITY OF THE INTERFACIAL POLYMER WITH RESPECT TO THE NUMBER OF SURFACE SITES, L.

As in Section II.A we consider a film of polymer, containing n_f chains, between two plates at distance h , exposed to bulk polymer at T and P_b . We have used the degrees of freedom $\{L, \{n_c\}, \{n_i^o\}\}$ to describe the microscopic state of this polymer. These degrees of freedom are not independent. They are related to each other, and to n_f , through the constraints, Eqs.(11) and (12). A set of independent degrees of freedom consists of L and the populations $\{n_c\}$ of all conformations but one. We are interested in calculating the derivative of the availability $\underline{r}_f$ with respect to L , keeping all other independent degrees of freedom constant.

An expression for the interfacial availability in terms of microscopic degrees of freedom is provided by Eq.(A.1). Using Eqs.(11) and (12), it can be rewritten as:

$$\begin{aligned} \frac{1}{kT} \underline{r}_f(T, P_b, n_f, a, h) = & -2mL \ln L + 2mL - (r-1) n_f \ln z + (r-1) n_f \ln L + \\ & + \sum_c n_c \ln \left(\frac{n_c}{\omega_c} \right) - \sum_c n_c + \sum_{i=1}^{2m} \left(L - \sum_c n_c r_{i,c} \right) \ln \left(L - \sum_c n_c r_{i,c} \right) - \\ & - \sum_{i=1}^{2m} \left(L - \sum_c n_c r_{i,c} \right) \\ & - x \sum_{i=1}^{2m} \left\{ \sum_c n_c r_{i,c} \left[\sum_{j=1}^{2m} \left(\lambda_{j-i} \frac{\sum_c n_c r_{j,c}}{L} \right) \right] \right\} - \end{aligned}$$

$$-\left(x_s + \lambda_1 x\right) \sum_c n_c \left(r_{1,c} + r_{2m,c}\right) + \sum_c n_c \left(\frac{\epsilon_c}{kT}\right) + 2mL \left(\frac{P_b v^*}{RT}\right) \quad (B.1)$$

Keeping all independent degrees of freedom constant is tantamount to keeping all $\{n_c\}$ constant in Eq.(B.1). The sought derivative, therefore, becomes:

$$\begin{aligned} \frac{1}{kT} \frac{\partial \gamma_f}{\partial L} \Big|_{\{n_c\}, T, P_b, h} &= -2m \ln L - 2m + 2m + \frac{(r-1)}{L} \left\{ \sum_c n_c \right\} + \\ &+ \sum_{i=1}^{2m} \ln \left[L - \sum_c n_c r_{i,c} \right] + 2m - 2m + \\ &+ \frac{x}{L} \sum_{i=1}^{2m} \left\{ \sum_c n_c r_{i,c} \left[\sum_{j=1}^{2m} \left(\lambda_{j-i} \frac{\sum_c n_c r_{j,c}}{L} \right) \right] \right\} + 2m \left(\frac{P_b v^*}{RT}\right) \end{aligned} \quad (B.2)$$

In view of Eqs.(12), (29) and (30), Eq.(B.2) gives:

$$\begin{aligned} \frac{1}{kT} \frac{\partial \gamma_f}{\partial L} \Big|_{\{n_c\}, T, P_b, h} &= \frac{(r-1)}{L} n_f + \sum_{i=1}^{2m} \ln \left[1 - \phi_i \right] + x \sum_{i=1}^{2m} \phi_i \langle \phi_i \rangle + \\ &+ 2m \left(\frac{P_b v^*}{RT}\right) \end{aligned} \quad (B.3)$$

Invoking Eq.(32) and the symmetry of the interfacial region, we rewrite Eq.(B.3) as

$$\begin{aligned}
\frac{1}{kT} \frac{\partial \tau_f}{\partial L} \bigg|_{\{n_c\}, T, P_b, h} &= 2 \left(1 - \frac{1}{r}\right) \sum_{i=1}^m \varphi_i + 2 \sum_{i=1}^m \left\{ x \varphi_i \langle \varphi_i \rangle + \ln(1 - \varphi_i) \right\} + \\
&+ 2m \left(\frac{P_b v^*}{RT} \right) \quad , \text{ which is Eq. (39), Q.E.D.}
\end{aligned}$$

APPENDIX C: INTERFACIAL MODEL EQUATIONS IN REDUCED NOTATION

Model equations, applicable to both the full equilibrium and the restricted equilibrium case, are collected here. The reduced probability notation, introduced in Eqs.(90) to (94) of the main text, is employed. The interfacial domain $1 \leq i \leq m$ is considered. Properties in the domain $m+1 \leq i \leq 2m$ are obtainable by symmetry.

(a) Equation of state for the bulk polymer:

$$\frac{P_b v^*}{RT} + \left(1 - \frac{1}{r}\right) \phi_b + \ln(1 - \phi_b) + x \phi_b^2 = 0 \quad (86)$$

(b) Reduced free segment probability-volume fraction relations:

$$p_1 = \left(\frac{1 - \phi_1}{1 - \phi_b}\right) \exp \left[2x \left[\langle \phi_1 \rangle - \phi_b \right] + \left[x_s + \lambda_1 x \right] \right] \quad (C.1)$$

$$p_i = \left(\frac{1 - \phi_i}{1 - \phi_b}\right) \exp \left[2x \left[\langle \phi_i \rangle - \phi_b \right] \right] \quad 2 \leq i \leq m$$

where

$$\left. \begin{aligned} \langle \phi_1 \rangle &= \lambda_0 \phi_1 + \lambda_1 \phi_2 \\ \langle \phi_i \rangle &= \lambda_1 \phi_{i-1} + \lambda_0 \phi_i + \lambda_1 \phi_{i+1} \\ \langle \phi_m \rangle &= \lambda_1 \phi_{m-1} + \left[\lambda_0 + \lambda_1 \right] \phi_m \end{aligned} \right\} \quad 2 \leq i \leq m-1 \quad (C.2)$$

(c) Conformation propagation equations:

$$\begin{array}{c}
 p(1,s) \\
 p(2,s) \\
 \vdots \\
 p(i,s) \\
 \vdots \\
 p(m-1,s) \\
 p(m,s)
 \end{array}
 =
 \begin{array}{cccccc}
 \lambda_0 \eta^0(1,s) p_1 & \lambda_1 \eta^-(1,s) p_1 & 0 & \cdot & \cdot & 0 \\
 \lambda_1 \eta^+(2,s) p_2 & \lambda_0 \eta^0(2,s) p_2 & \lambda_1 \eta^-(2,s) p_2 & \cdot & \cdot & \cdot \\
 0 & \cdot & \cdot & \cdot & \cdot & \cdot \\
 \cdot & \cdot & \lambda_1 \eta^+(i,s) p_i & \lambda_0 \eta^0(i,s) p_i & \lambda_1 \eta^-(i,s) p_i & \cdot \\
 \cdot & \cdot & \cdot & \cdot & \cdot & 0 \\
 \cdot & \cdot & \cdot & \cdot & \lambda_1 \eta^+(m-1,s) p_{m-1} & \lambda_0 \eta^0(m-1,s) p_{m-1} & \lambda_1 \eta^-(m-1,s) p_{m-1} \\
 0 & \cdot & \cdot & \cdot & 0 & \lambda_1 \eta^0(m,s) p_m & \left(\lambda_0 \eta^0(m,s) + \lambda_1 \eta^-(m,s) \right) p_m
 \end{array}
 \begin{array}{c}
 p(1,s-1) \\
 p(2,s-1) \\
 \cdot \\
 p(i,s-1) \\
 \cdot \\
 p(m-1,s-1) \\
 p(m,s-1)
 \end{array}$$

$$2 \leq s \leq r$$

(C.3)

where:

$$\eta^+(i,2) = \eta^0(i,2) = \eta^-(i,2) = 1$$

$$\eta^+(i,s) = \frac{1}{\tau^*} \frac{\lambda_1 p(i-2,s-2) + \lambda_0 \tau_L p(i-1,s-2) + \lambda_1 \tau_L p(i,s-2)}{\lambda_1 p(i-2,s-2) + \lambda_0 p(i-1,s-2) + \lambda_1 p(i,s-2)}$$

$$\eta^0(i,s) = \frac{1}{\tau^*} \frac{\lambda_1 \tau_L p(i-1,s-2) + \left((\lambda_0 - 2\lambda_1) \tau_L + \lambda_1 \tau_V + \lambda_1 \right) p(i,s-2) + \lambda_1 \tau_V p(i+1,s-2)}{\lambda_1 p(i-1,s-2) + \lambda_0 p(i,s-2) + \lambda_1 p(i+1,s-2)}$$

(C.4)

$$\eta^-(i,s) = \frac{1}{\tau^*} \frac{\lambda_1 \tau_V p(i,s-2) + \lambda_0 \tau_L p(i+1,s-2) + \lambda_1 p(i+2,s-2)}{\lambda_1 p(i,s-2) + \lambda_0 p(i+1,s-2) + \lambda_1 p(i+2,s-2)}$$

$$1 \leq i \leq m, \quad 3 \leq s \leq r,$$

$$\tau^* = \lambda_1 + \lambda_0 \tau_L + \lambda_1 \tau_V$$

(92)

and

$$p(i,1) = p_i$$

$$1 \leq i \leq m$$

$$p(-1,s) = p(0,s) = 0$$

$$p(m+1,s) = p(m,s); \quad p(m+2,s) = p(m-1,s)$$

$$2 \leq s \leq r$$

(C.5)

(d) Segment balance equations:

$$\phi_i = D \left(\frac{\phi_b}{r} \right) \frac{1}{p_i} \sum_{s=1}^r p(i,s)p(i,r-s+1) y(i,s) \quad 1 \leq i \leq m \quad (C.6)$$

where

$$y(i,1)=y(i,r)=1 \quad 1 \leq i \leq m$$

$$y(i,s) = \frac{1}{\psi(i,s)}^*$$

$$\begin{aligned} & \times \left\{ \lambda_1^2 p(i-1,s-1)p(i-1,r-s) \tau_V + \lambda_1 \lambda_0 p(i-1,s-1)p(i,r-s) \tau_L + \lambda_1^2 p(i-1,s-1)p(i+1,r-s) + \right. \\ & + \lambda_0 \lambda_1 p(i,s-1)p(i-1,r-s) \tau_L + \lambda_0 \left[\lambda_1 \tau_V + (\lambda_0 - 2\lambda_1) \tau_L + \lambda_1 \right] p(i,s-1)p(i,r-s) + \lambda_0 \lambda_1 p(i,s-1)p(i+1,r-s) \tau_L + \\ & \left. + \lambda_1^2 p(i+1,s-1)p(i-1,r-s) + \lambda_1 \lambda_0 p(i+1,s-1)p(i,r-s) \tau_L + \lambda_1^2 p(i+1,s-1)p(i+1,r-s) \tau_V \right\} \end{aligned}$$

$$\psi(i,s) = \tau^* \left[\lambda_1 p(i-1,s-1) + \lambda_0 p(i,s-1) + \lambda_1 p(i+1,s-1) \right] \left[\lambda_1 p(i-1,r-s) + \lambda_0 p(i,r-s) + \lambda_1 p(i+1,r-s) \right]$$

$$1 \leq i \leq m$$

$$2 \leq s \leq r-1$$

(C.7)

(d) In the full equilibrium model,

$$D=1$$

(99)

In the restricted equilibrium model, closure is provided by the additional equation:

$$\left(\frac{P_b^v}{RT} \right) + \frac{1}{m} \sum_{i=1}^m \left\{ \left(1 - \frac{1}{r} \right) \phi_i + \ln \left(1 - \phi_i \right) + x \phi_i \langle \phi_i \rangle \right\} \quad (112)$$

APPENDIX D: EQUIVALENCE OF THE DEFINITION, EQ.(102) TO PREVIOUS DEFINITIONS OF INTERFACIAL TENSION

We briefly show here that our definition of surface tension, in terms of the molar availabilities of the interfacial and bulk polymer, is consistent with previous theoretical approaches.

The thermodynamics of a fluid confined between two flat solid plates has been considered by Ash, Everett and Radke²¹ and, more recently, by Magda, Tirrell and Davis¹⁶. In the latter work a system consisting of s, f and b phases, analogous to the one chosen in Fig.5(b), is analyzed. We will use symbols without subscripts to denote total quantities (in phases s+f+b of the system); e.g., if $\underline{B}$ is an extensive quantity, such as volume, entropy, surface area, internal energy or availability,

$$\underline{B} = \underline{B}_f + \underline{B}_b + \underline{B}_s = n_f \underline{B}_f + n_b \underline{B}_b + n_s \underline{B}_s \quad (D.1)$$

The classical definition of interfacial tension is:

$$\gamma = \left. \frac{\partial \underline{U}}{\partial (2\underline{a})} \right|_{n, \underline{S}, \underline{V}, h} \quad (D.2)$$

By a straightforward thermodynamic analysis of infinitesimal changes in the state of the system¹⁶, one can derive the following fundamental representation for the total internal energy:

$$d\underline{U} = G_b dn + T d\underline{S} - P_b d\underline{V} - \left[P_N - P_b \right] d\underline{a} h + 2\gamma d\underline{a} \quad (D.3)$$

In Eq.(D.3), P_N is the normal pressure exerted by the film f on the plates. An external pressure ("disjoining pressure") of $P_N - P_b$ must be applied on them, pushing them towards each other, to keep their separation constant. G_b is the chemical potential of the fluid,

which, at full equilibrium, is the same in phases f and b.

By analogy to (D.2), one can define the surface tension of a clean solid (against vacuum) by:

$$\gamma_s = \left. \frac{\partial U_s}{\partial (2a_s)} \right|_{n_s, S_s, V_s} \quad (D.4)$$

It is assumed that the solid is incompressible, and that its spatial dimensions are not affected by the presence of adsorbed polymer. Thus, for a constant amount of solid n_s in the plates, the volume V_s is also constant, and the surface area a_s is the same as the contact area a in the presence of polymer. Changes in the internal energy, U_s , of the solid plates can result only from changes in S_s (reversible heat exchange) or a (change of plate shape, so that surface area is different):

$$dU_s = T dS_s + 2 \gamma_s da \quad (D.5)$$

Subtracting Eq.(D.5) from (D.3),

$$\begin{aligned} dU_f + dU_b = T [dS_f + dS_b] + G_b [dn_f + dn_b] - P_b [dV_f + dV_b] - \\ - [P_N - P_b] a dh + 2 [\gamma - \gamma_s] da \end{aligned} \quad (D.6)$$

Eq.(D.6) is a fundamental representation cast in terms of the extensive variables S , n , V , a and the intensive variable h .

By Euler integration¹⁷:

$$\begin{aligned} U_f + U_b = T [S_f + S_b] + G_b [n_f + n_b] - P_b [V_f + V_b] + 2 [\gamma - \gamma_s] a \\ \text{or} \\ 2 [\gamma - \gamma_s] a = [U_f - TS_f + P_b V_f] - n_f G_b + [U_b - TS_b + P_b V_b] - n_b G_b \end{aligned} \quad (D.7)$$

$$\text{But } \underline{U}_f - T\underline{S}_f + P_b\underline{V}_f = \underline{T}_f = n_f \underline{T}_f$$

(total availability of the interfacial polymer)

$$\text{and } \underline{U}_b - T\underline{S}_b + P_b\underline{V}_b = \underline{T}_b \equiv \underline{G}_b = n_b \underline{G}_b \equiv n_b \underline{T}_b$$

Hence,

$$2(\gamma - \gamma_s) \underline{a} = n_f (\underline{T}_f - \underline{G}_b) \equiv n_f (\underline{T}_f - \underline{T}_b)$$

which is Eq. (102), Q.E.D.

LIST OF SYMBOLS

a	: surface area
a^*	: area of a mole of surface sites; $a^* = N_L (\ell^*)^2$
b	: Kuhn segment length
D	: coefficient in expression for distribution of conformations defined in Eqs. (94), (95)
E	: potential energy
F	: augmented function in constrained optimizations
G	: Gibbs energy
h	: thickness of interfacial polymer film
h_s	: thickness of portion of phase s included in thermodynamic system
H	: intramolecular energy factor in conformation propagation equations, defined by Eqs. (54)
i	: index for lattice layers
k	: Boltzmann constant
$k(s,c)$	: number of layer in which segment s of conformation c finds itself
ℓ^*	: lattice edge length
L	: number of sites on each solid surface
m	: half number of layers in interfacial region
M	: chain molecular weight
n	: number of chains
n_{bi}^N	: number of bonds per surface site that connect layers i and $(i+1)$, and are therefore directed perpendicular to the interface
n_{bi}^L	: number of bonds per surface site that are directed parallel to the interface in layer i
n_c	: number of chains belonging to conformation c
n_i^O	: number of voids in layer i

- n_{si} : average number of segments per surface site that a chain passing through layer i has on that layer
- N_L : Avogadro number
- p : free or end segment probability in the interfacial region, reduced by its value in the unconstrained bulk
- $p_b(s)$: normalizing factor used in the calculation of bond order parameters, defined in Eq.(118)
- P : pressure
- P^* : Sanchez-Lacombe pressure parameter (characteristic pressure, indicative of the cohesive energy density of the polymer; equal to $(RT^*)/v^*$)
- P_i : "free segment probability" in layer i , defined in Eq.(35)
- P_* : asymptotic value of free segment probability in the bulk polymer
- $P(i,s)$: "end segment probability" for an s -segment long subchain in layer i , defined in Eq.(45)
- $P(s,i;r)$: "probability" that s -th segment of a chain r segments long is in layer i , defined in Eq.(43)
- $P(s,i;r)_c$: "probability" that s -th segment of a chain r segments long, belonging to conformation c , is in layer i , defined in Eq.(42)
- $P(r)$: chain "probability" (normalization factor), defined in Eq.(41)
- $P(r)_c$: "probability" of conformation c , defined in Eq.(40)
- $\vec{p}(i)$: vector of free segment probabilities for chain not passing through layer i , defined in Eq.(123)
- $\vec{p}(i)(s)$: vector of end segment probabilities for subchains of length s not passing through layer i , defined in Eq.(125)
- $\vec{p}(i)(r)$: reduced chain probability for chains not passing through layer i , defined in Eq.(126)
- r : chain length (segments)
- $r_{i,c}$: number of sites occupied by conformation c in layer i

- R : ideal gas constant; also, radial distance
 s : index for segments and bonds along a chain
 s_I, s_L, s_V : number of bond pairs in trans, gauche and backstepping conformational state within a chain
 S : entropy
 S_i : bond order parameter in layer i
 t : continuous variable, indicative of segment position along a chain
 T : temperature
 T^* : Sanchez-Lacombe temperature parameter (characteristic temperature of segment-segment interactions; $T^* = - \frac{z w_{AA}}{2k}$)
 T_L : temperature characteristic of the intramolecular energy associated with the gauche placement of a bond, relative to trans
 T_V : temperature characteristic of the intramolecular energy associated with bond backstepping, relative to trans placement
 T_S^* : characteristic temperature of segment/surface interactions; $T_S^* = - \frac{w_{AS}}{k}$
 $u(z)$: "self consistent field" free energy function in continuum formulation, defined in Eq.(141)
 $u_{AA}(R)$: attractive potential of segment-segment interactions in continuum formulation
 $u_{AS}(R)$: attractive potential of adsorptive segment-surface interactions in continuum formulation
 U : internal energy
 v^* : volume of one mole of chain segments; $v^* = N_L (\ell^*)^3$
 V : volume
 w : potential energy of segment/segment or segment/surface interactions, per pair of adjacent lattice sites
 $\underline{w}$: chain conformation propagation matrix, defined in Eq.(122)
 x : coordinate axis parallel to interface

- y : coordinate axis parallel to interface
 $y(i,s)$: reduced intramolecular energy factor in segment balance equations, defined in Eq.(C.7)
 $Y(i,s)$: intramolecular energy factor in segment balance equations, defined in Eq.(59)
 z : lattice coordination number; $z=6$
 also: coordinate axis perpendicular to interface

Greek Symbols

- γ : surface tension of pure polymer; interfacial tension in polymer/solid system
 γ_s : surface tension of clean solid
 δ : solubility parameter
 δ_f : distance, over which variations in polymer structure at the interfacial region are observed
 δ_{ij} : Kronecker delta
 ϵ : intramolecular (conformational) potential energy for a pair of adjacent bonds along a chain, relative to trans placement
 ϵ_c : total intramolecular (conformational) energy of a chain in conformation c
 $\bar{\epsilon}_c$: mean conformational free energy of a chain in the bulk polymer
 ζ_i : Lagrange multiplier associated with segment balance constraint in layer i , defined in Eq.(24)
 η : reduced intramolecular energy factors in conformation propagation equations, defined by Eqs.(C.4)
 λ_0 : fraction of nearest-neighbor sites to a given site lying in same layer as the considered site
 λ_1 : fraction of nearest-neighbor sites to a given site lying in layer above (i.e. nearer the surface) the layer of the considered site;
 also, fraction of nearest-neighbor sites to a given site lying in layer below the layer of the considered site

μ	: chemical potential
ξ	: Lagrange multiplier associated with chain balance constraint, defined in Eq.(24)
ρ	: polymer mass density
ρ_b^*	: hard core density of polymer
$\rho_i(s)$	: contribution to density of polymer in layer i due to segments of order s
τ	: Boltzmann factor, corresponding to the energy of a conformational state
τ^*	: Boltzmann factor corresponding to the average conformational free energy per bond pair in the bulk, defined by Eq.(92)
φ	: polymer volume fraction
$\varphi_i(s)$	: contribution to volume fraction of polymer in layer i due to segments of order i
χ	: segment-segment interaction parameter, defined in Eq.(26)
χ_s	: segment-surface interaction parameter, defined in Eq.(26)
$\psi(i,s)$	: normalizing factor used in accounting for intramolecular energy contributions in the segment balance equations, defined by Eq.(C.7)
γ	: availability [thermodynamic property, defined in Eq.(5)]
ω_c	: factor proportional to the number of arrangements of conformation c on the lattice, defined in Eq.(9)
Ω	: number of ways of arranging a given set of conformations and voids in the lattice

SUPERSCRIPTS

intra	: intramolecular
L	: bond direction parallel to interface
N	: normal bond direction (perpendicular to interface)
+	: forward propagation of conformation (away from interface)

- : backward propagation of conformation (away from interface)
- o : void
- 0 : propagation of conformation in same layer

SUBSCRIPTS

- A : polymer segment
- b : unconstrained bulk polymer phase;
bond
- f : interfacial polymer (film) phase
- fj : freely jointed chain
- i : lattice layer index
- I : trans placement of a bond relative to previous bond
- intra : intramolecular
- L : gauche placement of a bond relative to previous bond
- N : normal component of pressure
- s : nonpolymer (solid or gaseous) phase;
segment index
- sb : bulk solid, in the absence of surfaces
- S : surface site
- T : transverse component of pressure
- V : backstepping placement of a bond relative to previous bond

SPECIAL SYMBOLS

$_$ (underbar): total (as opposed to molar or specific) extensive thermodynamic quantity

$\langle \ \rangle$: ensemble average; spatial average

FIGURE CAPTIONS

Figure 1: Model system considered in this work, and definition of the solid (or gas), interfacial polymer and bulk polymer phases.

Figure 2: Lattice conformational states, and their characteristic energies

Figure 3: Terminal conformations of an s -long subchain, having its last segment in layer i . These conformations are considered in developing the recursive conformation propagation equations of Section II.B.

Figure 4: Separation of a chain into two subchains, for formulating the segment balance equations.

Figure 5: Selection of the thermodynamic system for (a) full equilibrium analysis; (b) restricted equilibrium analysis.

Figure 6: Decomposition of a chain around bond s , used in the calculation of bond orientation characteristics.

Figure 1

Figure 2

Segm. s in layer i

Segm. (s-1) in layer (i-1):				i-2 i-1 i
No. of configs.:	$\lambda_1 z$	$\lambda_0 z$	$\lambda_1 z$	
Energy:	0	ϵ_L	ϵ_V	

Segm. (s-1) in layer i:						i-1 i i+1
No. of configs.:	$\lambda_1 z$	$(\lambda_0 - 2\lambda_1) z$	$\lambda_1 z$	$\lambda_1 z$	$\lambda_1 z$	
Energy:	ϵ_L	ϵ_L	0	ϵ_V	ϵ_L	

Segm. (s-1) in layer (i+1):				i i+1 i+2
No. of configs.:	$\lambda_1 z$	$\lambda_0 z$	$\lambda_1 z$	
Energy:	0	ϵ_L	ϵ_V	

Figure 3

Figure 4

Figure 5

Figure 6