Concentrated Polymer Solution Between Plates

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Synopsis

Geometric requirements, avoidance of boundary conditions, and focus on configurational properties have suggested mean field formulation of the many chain problem using discrete single chain Gaussian partition functions. Mean field account of energetic, combinatorial, and configurational contributions to the free energy provides correct reduction in the limit of remote confinement and avoidance of double counting of interactions. Strong influence of surface adsorption on configurational and global properties of spatial distribution is predicted to occur at lower concentrations. The interplate surface tension has been calculated in decoupled conditions (large separation distances between plates). Numerical results predict an approximate power law dependence of the surface tension on the concentration with exponent ~ 1.3. Perfectly repulsive boundaries and athermal solvent conditions have been assumed for this calculation.

INTRODUCTION

The mean field analysis of polymer systems between plates has followed three main lines so far: (1) lattice models,[1-4] (2) effective single chain statistical approaches,[5,6] and (3) variational treatments.[7,8] The second approach is more suitable for the investigation of configurational properties, i.e., end-to-end distances, radii of gyration, and scattering functions. Classical treatments[5,6] using the diffusion equation formalism must define the boundary conditions *a priori*. Therefore, we have decided to reformulate the problem in terms of confined Gaussian partition functions. The existence of rigid boundaries suggests proper choices for the spacing between successive beads, as we will see. Mean field treatments are useful for concentrated systems. Furthermore, thermodynamic equilibrium with the bulk solution has to be investigated properly. To this extent, a satisfactory account of translational, combinatorial, and energetic degrees of freedom must both provide reduction to Flory–Huggins form in the unconfined limit and possible separation of combinatorial from energetic effects, leading to different forms of the respective free energy functionals of the density profile, as we will see. Avoidance of improper counting of interactions requires also "bare" redefinition of the configurational term of the free energy. All these features are discussed in the following sections. The calculated density profile does not vanish in the vicinity of the plates and tends to uniformity at higher densities. Correct formulation of boundary conditions, configurational restrictions, and results obtained for density profile and surface tension confirm the general validity of our proposed method. Configurational contributions are predicted to dominate the surface tension of sharply confined solutions. In the case of surface adsorption, the predicted dependence of the density profile on the monomer adsorption

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energy is remarkably sharp at low concentrations as expected from single chain systems. A model system of 22 Gaussian beads has been used for all calculations.

PACKING ENTROPY AND ENTHALPY OF DENSE POLYMER CHAIN SYSTEMS BETWEEN PLATES

In this section, we evaluate the combinatorial entropy of a set of chains having prescribed position and configuration between fixed plates. Counting of possible configurations and calculation of energetic contributions have to be done in separate steps, consistently with a given assumed profile of the volume fraction, $\phi(x)$. The translational degrees of freedom are conveniently shifted from the packing to the configurational term of the free energy in order to simplify proper account of geometric requirements. The combinatorial partition function Z_1 is

$$Z_1 = \frac{1}{n_p!} \prod_{i=1}^{n_p - 1} Z_{i+1}\{\phi_i(x)\} \tag{1}$$

where n_p is the number of molecules and x ranges between $-L/2$ and $L/2$, L being the plate separation distance. The chains are placed into the lattice sequentially and $\phi_i(x)$ is the profile of the polymer volume fraction seen by the $(i + 1)$th chain. We assume $\phi_i(x) = (i/n_p)\phi(x)$. Equation (1) holds for assigned configurations of all the chains. If the density is constant, each factor must be completed by adding its configurational degeneracy, not influenced by interactions with the environment. However, in the presence of inhomogeneous concentration fields, the release of configurational degrees of freedom yielding the corresponding term of the free energy must be allowed on the fully packed system only. This difference from homogeneous systems legitimizes separation of steps. The individual contributions are

$$Z_{i+1}\{\phi_i(x)\} = \prod_{j=1}^{N_c}\left[1 - \frac{i}{n_p}\phi(x_j)\right] \tag{2}$$

where N_c is the number of *statistically independent* packing units of the general chain. N_c does not coincide with N, the total number of independent *configurational units*, especially in the presence of rigid boundaries posing severe restrictions to scaling freedom. The sets x_i and $\phi(x_i)$ change discontinuously from one chain to the next. Averaging over a convenient number of successive steps, we may write

$$\overline{\ln Z_{i+1}} = \frac{N_c}{v_p L}\int_{-L/2}^{L/2}\phi(x)\ln\left[1 - \frac{i}{n_p}\phi(x)\right]dx, \tag{3}$$

where v_p is the average polymer volume fraction of the complete system.

Integrating over i, we obtain the final formula

$$\ln Z_1 = -\ln(n_p!) - n_p N_c - \frac{n_p N_c}{v_p L} \int_{-L/2}^{L/2} dx [1 - \phi(x)]\ln[1 - \phi(x)] \quad (4)$$

v_p being the average volume fraction between the plates. Equation (4) does not provide a packing entropy proportional to the number of chains. Proper reduction to correct thermodynamic behavior is obtained adding the configurational term. Evaluation of the energetic term yields the corresponding enthalpy. Introduction of the $(i + 1)$th chain comprising N_c lattice cubes implies elimination of N_c effective solvent molecules. The resulting change of the energy of the system is

$$\frac{\Delta E_{i+1}}{kT} = \sum_{j=1}^{N_c} \left\{ \chi_{PS}^c \left[1 - \frac{2i}{n_p}\phi(x_j) \right] + \chi_{PP}^c \frac{i}{n_p}\phi(x_j) + \chi_{SS}^c \left[\frac{i}{n_p}\phi(x_j) - 1 \right] \right\}$$

$$(4a)$$

with all the χ's describing cube–cube interactions. Averaging over a convenient number of successive steps, we obtain

$$\overline{\frac{\Delta E_{i+1}}{kT}} = \frac{N_c}{v_p L} \int_{-L/2}^{L/2} dx\, \phi(x) \left\{ \chi_{PS}^c \left[1 - \frac{2i}{n_p}\phi(x) \right] + \chi_{PP}^c \frac{i}{n_p}\phi(x) \right.$$

$$\left. + \chi_{SS}^c \left[\frac{i}{n_p}\phi(x) - 1 \right] \right\} \quad (4b)$$

Integrating over i and rescaling the χ's to the chain monomer, the enthalpy ΔH becomes

$$\frac{\Delta H}{kT} = n_p N_m \left(\chi_{PS} - \frac{V_m}{V_c}\chi_{SS} \right) - \frac{n_p \bar{\chi} N_m}{v_p L} \int_{-L/2}^{L/2} \phi^2(x)\, dx \quad (5)$$

where $\bar{\chi} = \chi_{PS} - [\chi_{PP} + \chi_{SS}(V_m/V_c)]/2$ is the effective monomer interaction parameter[9,10] and N_m is the number of monomers per chain. V_c and V_m are lattice cube volume and monomer volume, respectively. The size of the lattice cube and the number of monomers per lattice cube are naturally dictated by the geometry of the polymer. For simplicity, each effective solvent molecule is assumed to fill exactly one lattice cube. Equation (4) becomes also quadratic in $\phi(x)$ at small concentrations. The distinction between number of monomers, number of lattice cubes, and number of configurational strands per chain implies simple scaling laws for the related energetic, configurational, and steric parameters. For sufficiently long chains containing N beads, we consider the configurational partition function

$$Z_{conf} = Z_x^{n_p} Z_y^{n_p} Z_z^{n_p} \quad (6)$$

where

$$Z_x = \frac{1}{a} \int \int \int_{-L/2}^{L/2} \int \prod_{i=1}^{N} dx_i \exp\left[-\frac{C}{2kT} \prod_{i=1}^{N-1} (x_{i+1} - x_i)^2 \right] \cdot \exp\{U(\{\phi\})\} \quad (7)$$

where $3\ kT/C$ is the average square distance between consecutive beads and

$$U(\{\phi\}) = \sum_{i=1}^{N} \left\{ \sigma_G \ln\left(\frac{1 - \phi(x_i)}{1 - v_p} \right) + (\chi_{\text{eff}}^G)[\phi(x_i) - v_p] \right\} \quad (8)$$

accounts for both steric and energetic interactions due to inhomogeneity of the environment; σ_G is the number of cubes per *Gaussian strand* and χ_{eff}^G characterizes the effective energetic interaction of a strand with its environment. Equation (4.1) consistently requires that $\chi_{\text{eff}}^G = 2\bar{\chi}^G$, where $\bar{\chi}^G$ is the already defined monomer interaction parameter, multiplied by the number of monomers contained in each strand. Use of eq. (7) to investigate single chain statistics in θ conditions ($\bar{\chi}^c = \frac{1}{2}$) at moderate concentrations confirms this result independently.

Z_y and Z_z have ideal Gaussian form. The length a defines the size of the statistical cube of the lattice. From eqs. (6) and (7) we obtain in the case of large L, with mostly uniform density profiles,

$$\ln Z_{\text{conf}} = n_p \ln n_0 + n_p \ln Z_c \quad (9)$$

where n_0 is the total number of lattice sites and $\ln Z_c$ has the ideal Gaussian form. The term $n_p \ln n_0$, subtracted from eq. (9) and added to eq. (4), reestablishes its correct thermodynamic limit and yields the Flory–Huggins expression for the packing entropy in the case of large separation between plates. Transfer of $n_p \ln n_0$ to the packing term is done by redefining the x component of the partition function as $\tilde{Z}_x = (a/L)Z_x$. With this change, $\tilde{Z}_x$ tends to $Z_c^{1/3}$ as $L \to \infty$, therefore allowing direct comparison with the chains of the bulk solution. For finite plate separation, eq. (7) includes contributions due to steric and energetic interaction with the medium, already accounted for in eqs. (4) and (5). Further subtraction of the ideal term $-n_p \ln Z_c$ yields the effective configurational free energy

$$\frac{F_{\text{conf}}}{kT} = -n_p \ln\left[\tilde{Z}_x / Z_c^{1/3} \right] + n_p \langle U(\{\phi\}) \rangle \quad (10)$$

F_{conf} vanishes for large separation between plates. Equation (10), corresponding to the "bare" redefinition mentioned in the Introduction, represents the average change of configurational free energy experienced by the chains because of plate confinement. Equation (7) expresses the partition integral in Gaussian form. The size of the Gaussian unit must be chosen conveniently. In the vicinity of a plate, avoidance of forbidden internal crossings is approximately guaranteed choosing a separation of the order of the Kuhn segment between successive beads, because shorter strands do not obey Gaussian statistics. More intuitive formulation of the problem can be made as follows.

The dimension of a Gaussian coil is of the order of the radius of gyration. If the subcoil persistence length is smaller than its size, a substantial number of internal configurations leave both extremes on the right side of the plate, pushing parts of the submolecule inside the forbidden region. Imposing a condition of quantitative correspondence between coil radius and persistence length, a reasonable compromise between configurational accuracy and obedience to constraints is reached. Using known expressions for radius of gyration and persistence length,[11]

$$n_b \simeq \frac{3}{2} \frac{(C_\infty + 1)^2}{C_\infty} \tag{11}$$

i.e., $n_b \simeq 20$ bonds for polystyrene. We conclude this section giving the final expression of the packing entropy:

$$\ln Z_1 = n_p \ln\left(\frac{N_c}{v_p}\right) + n_p(1 - N_c)$$

$$- \frac{n_p N_c}{v_p L} \int_{-L/2}^{L/2} dx \, [1 - \phi(x)]\ln[1 - \phi(x)]$$

which reduces to standard Flory–Huggins form in the limit $L \to \infty$.

SELF-CONSISTENT EVALUATION OF THE PROFILE OF THE VOLUME FRACTION $\phi(x)$

Introducing the reduced variables $u_i = x_i\sqrt{C/2kT}$ and the dimensionless quantity $b = (L/2)\sqrt{C/2kT}$, we obtain the following expression for $\tilde{Z}_x$:

$$\tilde{Z}_x = \frac{1}{2b} Z_c^{1/3} \langle \exp(\psi) | \hat{K}^{N-1} | 1 \rangle, \tag{12}$$

where

$$\hat{K}|f\rangle = \frac{1}{\sqrt{\pi}} \int_{-b}^{b} \exp\left[-(u-v)^2\right] \exp[\psi(v)] \, f(v) \, dv \tag{13}$$

with

$$\psi(v) = \sigma_G \ln\left[\frac{1 - \phi(v)}{1 - v_p}\right] + (2\bar{\chi}^G)\left[\phi(v) - v_p\right] \tag{14}$$

The operator $\hat{K}$ does not have a symmetric Kernel. Equation (12) can be symmetrized introducing the operator $\hat{Q}$ defined by the equation

$$\hat{Q}|f\rangle = \frac{1}{\sqrt{\pi}} \int_{-b}^{b} \exp\left[-(u-v)^2\right] \exp\left[\tfrac{1}{2}\psi(u) + \tfrac{1}{2}\psi(v)\right] f(v) \, dv \tag{15}$$

so as to obtain

$$\tilde{Z}_x = \frac{1}{2b} Z_c^{1/3} \langle \exp(\psi/2)|\hat{Q}^{N-1}|\exp(\psi/2)\rangle \tag{16}$$

The bead density $\rho(u)$ can be expressed as

$$\rho(u) = \left\langle \sum_{p=1}^{N} \delta(u - u_p) \right\rangle \tag{17}$$

This average must be calculated using the partition function. We obtain

$$\rho(u) = \sum_{p=1}^{N} \frac{\langle \exp(\psi/2)|\hat{Q}^{p-1}\delta(u - u_p)\hat{Q}^{N-p}|\exp(\psi/2)\rangle}{\langle \exp(\psi/2)|\hat{Q}^{N-1}|\exp(\psi/2)\rangle} \tag{18}$$

Comparison with eq. (7) shows that iterated applications of the operator are done decreasing the order of the addressed variable. Introducing the function $g(u, s)$ by the equation

$$g(u, s) = \hat{Q}^s|\exp(\psi/2)\rangle \tag{19}$$

and using the symmetry property

$$\langle f |\hat{Q}^m|g \rangle = \langle g|\hat{Q}^m| f \rangle \tag{20}$$

we obtain the simple formula

$$\rho(u) = \frac{\displaystyle\sum_{p=1}^{N} g(u, p - 1)g(u, N - p)}{\displaystyle\int_{-b}^{b} \exp(\psi/2)g(v, N - 1)\, dv} \tag{21}$$

Equation (21) satisfies the condition

$$\int_{-b}^{b} \rho(u)\, du = N \tag{22}$$

Proper normalization gives the total volume fraction $\phi(u)$

$$\phi(u) = (2bv_p/N)\rho(u) \tag{23}$$

Being a volume fraction, $\phi(u)$ is *invariant* with respect to the transformation $x \to u$ $[\phi(x) = \phi(u)]$. The profile of the volume fraction $\phi(x)$ must obey self-consistency requirements. Numerically, we have solved the problem by increasing the overall volume fraction gradually from dilute conditions, with extended sequential stabilization. Final concentrations of about 90% have been easily obtained in this way so far. Evaluation of $g(u, s)$ can be done numerically by successive applications of the operator, whose proper normal-

ization (division by $\sqrt{\pi}$ and calibration of interactive terms to register only deviations from the average concentration) avoids extreme numerical conditions, to large order of iteration. We have considered a few practical cases to illustrate trends which are probably general. Increasing concentration forces the profile to become more even, therefore raising the segment density in the vicinity of the plates. In the dilute limit, this concentration tends to vanish, as assumed by diffusion equation calculations.[5] Finite boundary densities have also been reported by authors employing the lattice model.[2,13] As a significant example, we have chosen a polymer molecule of 22 beads, assuming that each strand can be decomposed into 3.3 statistical cubes. Geometric considerations and eq. (11) suggest identification with 20,000 MW polystyrene. In the case of polystyrene, $\sigma = 3.3$ corresponds to having about 3 monomers per lattice *cube*, in approximate agreement with requirements of isotropic granularity. We have considered $b = 5$ to study interplate confinement and $b = 25$ for the analysis of surface tension in decoupled conditions. In the case of polystyrene, $b = 5$ corresponds to a plate separation of about 168 Å, with a comparable unperturbed $\sqrt{\langle r^2 \rangle}$ of 100 Å. Athermal conditions ($\bar{\chi} = 0$), as stated previously, are assumed in this paper. Suitable scattering experiments provide a viable opportunity for measurement of size and detection of internal correlations of labeled chains. Within our mean field approximation, orthogonal components of the partition function are decoupled. Radii of gyration, rms distances between extremes, and special cases of the scattering function can be evaluated from the partition integral introducing virtual external fields.

CHAIN DIMENSIONS AND SINGLE CHAIN SCATTERING FUNCTION

The x component of the radius of gyration $\langle S_x^2 \rangle$ is defined by the equation

$$\frac{C}{2kT}\langle S_x^2 \rangle = \frac{1}{N}\sum_{i=1}^{N}(u_i - u_G)^2 \tag{24}$$

where u_G is the center of mass coordinate. Expressing u_G in terms of the u_i, we rewrite eq. (24) as

$$\frac{C}{2kT}\langle S_x^2 \rangle = \frac{1}{N}\sum_i \langle u_i^2 \rangle - \frac{1}{N^2}\sum_{j,k}\langle u_j u_k \rangle \tag{25}$$

Focusing first on the second term, we observe that it contains too many pairs (j, k). Using eq. (12), we can express $\sum_{j,k}\langle u_j u_k \rangle = (\sum_j u_j)^2$ as

$$\sum_{j,k}\langle u_j u_k \rangle = \frac{\partial^2}{\partial \epsilon^2}\left\{\frac{\langle \exp[\psi(u) + \epsilon u]\,\hat{P}^{N-1}|1\rangle}{\langle \exp(\psi)|\hat{K}^{N-1}|1\rangle}\right\}_{\epsilon=0} \tag{26}$$

where

$$\hat{P}f = \frac{1}{\sqrt{\pi}}\int_{-b}^{b}\exp[-(u-v)^2]\exp[\psi(v) + \epsilon v]\,f(v)\,dv \tag{27}$$

Analogous and more intuitive procedure can be used for the calculation

$\sum_i \langle u_i^2 \rangle$. All derivatives with respect to the virtual parameter can be calculated numerically to a satisfactory degree of accuracy. Restricting virtual influence to the extremes, the mean square end-to-end distance is generated. Calculation of the scattering function presents more complex problems, due to coupling between different components of the position vectors. The case of scattering vectors parallel to the plates is ideal, within our configurational and statistical approximations valid for concentrated systems. For scattering vectors perpendicular to the surfaces, a simple mathematical procedure can be developed, similar to that used for the evaluation of the radius of gyration. From the definition

$$S(\mathbf{Q}) = \frac{1}{N^2} \sum_{m,j} \left\langle \exp\left[iQ_x(x_m - x_j)\right]\right\rangle \tag{28}$$

simple calculations yield

$$S(\mathbf{Q}) = S_1(Q_x) + S_2(Q_x) \tag{29}$$

with

$$S_1(Q_x) = \frac{1}{N^2} \left\langle \left[\sum_i \cos(Q_x x_i)\right]^2 \right\rangle \tag{30}$$

$$S_2(Q_x) = \frac{1}{N^2} \left\langle \left[\sum_i \sin(Q_x x_i)\right]^2 \right\rangle \tag{31}$$

Introducing the quantity $\Gamma = Q_x\sqrt{2kT/C}$, we obtain

$$S_1(\Gamma) = \frac{1}{N^2} \frac{\partial^2}{\partial \epsilon^2} \left\{ \frac{\langle \exp[\psi(u) + \epsilon \cos(\Gamma u)] | \hat{G}^{N-1} | 1\rangle}{\langle \exp[\psi(u)] | \hat{K}^{N-1} | 1\rangle} \right\}_{\epsilon = 0} \tag{32}$$

with

$$\hat{G}f = \frac{1}{\sqrt{\pi}} \int_{-b}^{b} \exp\left[-(u-v)^2\right] \exp[\psi(v) + \epsilon \cos(\Gamma v)] f(v)\, dv \tag{33}$$

Extension to the calculation of $S_2(Q_x)$ is straightforward. As before, numerical evaluation of the double derivative is easily accessible with and without surface adsorption.

Distinction between reversible and permanent adsorption is often discussed in the literature.[8] Final classification requires balance of all variables potentially altered by probing equilibrium conditions (separation between plates and concentration, specifically). Within the general framework of our approach, we account for adsorption introducing potential wells at the two surfaces. Two parameters are needed: depth and related width of the poten-
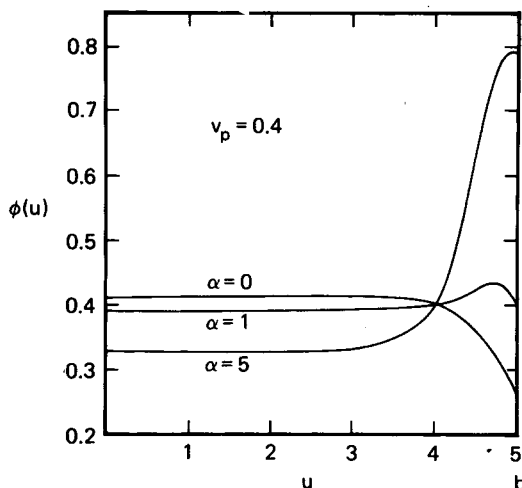
Fig. 1. Polymer volume fraction ϕ vs. reduced distance u from the interplate center for $\alpha = 0$, 1, and 5. Average volume fraction and plate distance are $v_p = 0.4$ and $2b = 10$, respectively. A model chain of 22 beads ($\sim$ 20 K PS) is considered in all examples.

tial well, assumed to be of semi-Gaussian form for all strands:

$$V = -\alpha kT \exp(-z\Delta u)^2 \tag{34}$$

where Δu is the distance from the surface, normalized according to the definition of the reduced variable u used in eqs. (12) and (13). We have chosen configurational strands of the order of the Kuhn segment. Therefore, effective interaction between plate and statistical unit must extend to a distance comparable with its size. To this extent, values of z of order unity are
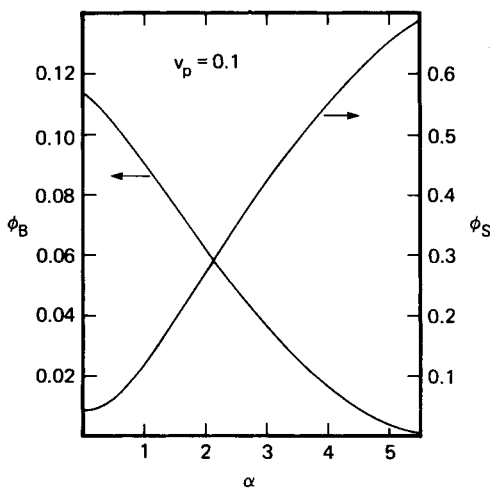

Fig. 2. Polymer volume fractions in the intermediate region between the plates (ϕ_B) and at the adsorption surfaces (ϕ_s) vs. adsorption energy α. Average volume fraction and plate distance are $v_p = 0.1$ and $2b = 10$, respectively.

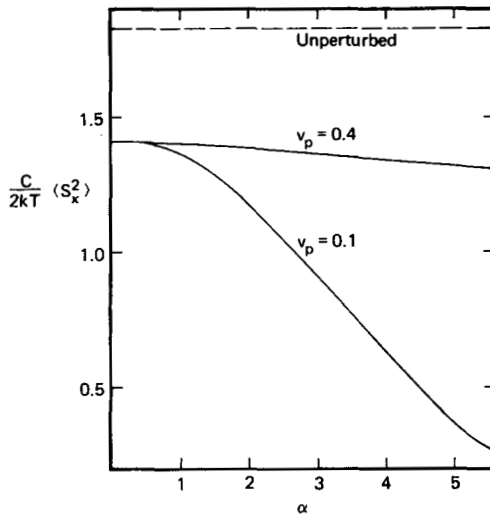Fig. 3. Transverse components of the radius of gyration $\langle S_x^2 \rangle$, for $v_p = 0.1$ and 0.4.

physically meaningful. We have taken $z = 3$. Two significant concentrations have been considered: $v_p = 0.1$ and 0.4. In each case, α has been varied over a substantial range. For $v_p = 0.1$, the value $\alpha \simeq 1$ (corresponding to an adsorption energy of about 0.1 kT per monomer) appears to be sufficient for compensation of surface depletion and flattening of density profile. At $\alpha \simeq$ 3.5–4, migration of polymer matter toward the surfaces increases sharply, leaving the interplate region at concentration levels orders of magnitude smaller than the average value v_p. In most experiments,[12] the average inter-plate concentration may change with α (i.e., temperature). Keeping it fixed is experimentally conceivable. For $b = 5$, Figure 1 shows the density profile at different values of the adsorption constant with a global concentration of $v_p = 0.4$. u is the normalized distance from the center of the interplate region.
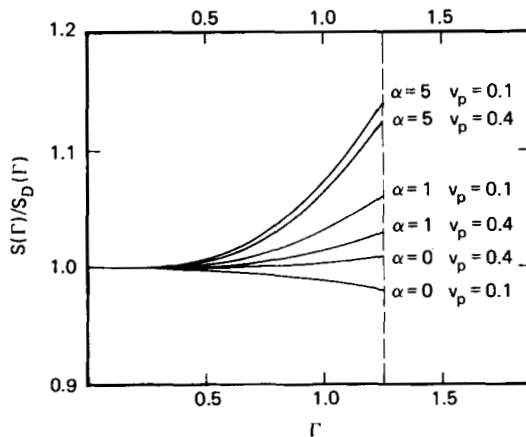

Fig. 4. Normalized scattering function $S(\Gamma)$ for different values of v_p and α. $S_D(\Gamma)$ is the Debeye function of corresponding to the true value of $\langle S_x^2 \rangle$.

Figure 1 shows that the depletion (adsorption) layer has a size which does not depend on the intensity of the adsorption constant and is determined principally by the dimension of the configurational unit. The influence of surface adsorption on the interplate concentration is much more dramatic at low global concentrations, as mentioned before. For $v_p = 0.1$, surface volume fraction ϕ_s and interplate concentration ϕ_B are reported in Figure 2. Figure 3 shows the dependence of the radius of gyration $\langle S_x^2 \rangle$ on the adsorption constant α, with $b = 5$: insensitivity at $v_p = 0.4$ and dramatic decrease at the lower concentration $v_p = 0.1$, as expected from single chain systems.[14] The scattering function $S(\Gamma)$ is plotted in Figure 4 at the two concentrations, for several values of α. $S_D(\Gamma)$ is the Debeye function, constructed using the true value of the radius of gyration $\langle S_x^2 \rangle$. Values of Q_x higher then 0.1 Å^{-1} have not been considered, because discrete Gaussian models fail in those conditions.

CALCULATION OF SURFACE TENSION

Surface tension is another property of confined polymer systems which requires specific reference to the polymer persistence length. The case of polymer surfaces bounded by media of low entropic and energetic exchange activity can be dealt with, assuming the existence of effective boundary surfaces. Separation of the total free energy into bulk term and surface contribution provides the operational definition of the surface tension. In the case of polymer systems between plates, we may apply this definition evaluating the total free energy per unit area, subtracting the uniform contribution, letting the plate separation go to infinity, and dividing by 2. In practice, our numerical approach requires large plate distances: $L \sim 8\text{--}9\sqrt{\langle r^2 \rangle}$ reduces the positive extra free energy of interaction to relative fractions of about one percent. Application of eqs. (4), (5), and (10) gives the three separate extra terms of the free energy, interpretable as surface contributions arising from the plate regions. Reduction to unit area is done by the formula

$$n_p N V_G = v_p L A \qquad (35)$$

where V_G is the volume per bead and A the plate area. The surface tension γ becomes

$$\gamma = \frac{kT}{2V_G} \left(\frac{2kT}{C} \right)^{1/2} \Gamma_s \qquad (35')$$

where Γ_s is dimensionless:

$$\Gamma_s = \frac{2v_p b}{N} \left[\langle U(\{\phi\}) \rangle - \ln(\tilde{Z}/Z_c^{1/3}) \right]$$

$$- \bar{\chi} n_m \int_{-b}^{b} \left[\phi^2(u) - v_p^2 \right] du + \sigma_G \int_{-b}^{b} du$$

$$\times \left\{ [1 - \phi(u)] \ln[1 - \phi(u)] - (1 - v_p)\ln(1 - v_p) \right\} \qquad (36)$$
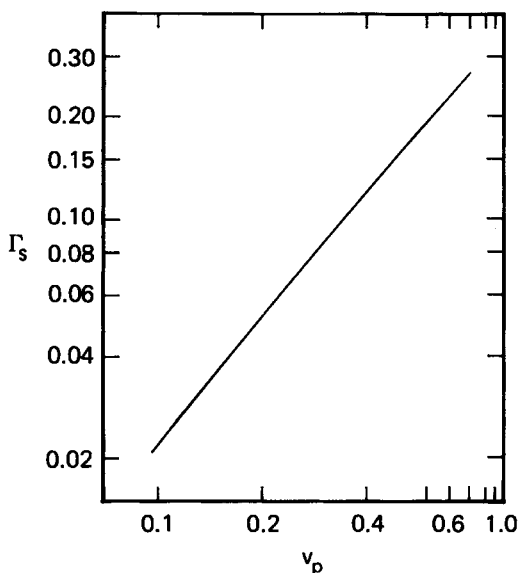
Fig. 5. Dimensionless surface tension Γ_s calculated as a function of concentration for $b = 25$ and perfectly repulsive boundaries.

n_m being the number of monomers per Gaussian strand, since $\bar{\chi}$ is defined with respect to the monomer unit. $\tilde{Z}/Z_c^{1/3}$ is obtained from eq. (12). For purposes of calculation the finite value $b = 25$ is sufficient. Energetically indifferent mixing has been assumed (good solvent). Practical calculations on our model polymer containing 22 beads cover the range $v_p = 0.1$–0.85. The configurational contribution appears to dominate at all concentrations. Preadjustment of the density baseline enveloping the interactive terms reduces the correction contained in eq. (10) to deceivingly small values of about 20%, even at the higher concentrations. Calculated values of Γ_s are reported in Figure 5. The slope of this curve is $\simeq 1.31$. For strands of 20 PS bonds, $V_G \simeq 1800$ Å^3. Taking $T = 300$ K, and using configurational data ($C_\infty \simeq 10$), we obtain $\gamma \simeq 2\Gamma_s$ (erg/cm^2). Extrapolation of our results to the bulk and multiplication by two gives $\gamma \simeq 1$–2 erg/cm^2. Comparison with demixed polymer data[15] is only indicative, because of finite interfaces[16] and mismatch of compressibility. Remarkably, the indication appears to be quantitatively correct in the case of PMMA and PS, whose separate γ's are almost identical.[15] Perfectly repulsive boundaries have been assumed in this calculation. Doubling of molecular weight (44 beads) does not introduce relevant changes of Γ_s.

DISCUSSION

Our molecular treatment of plate adsorption and surface tension uses finite sizes of the Gaussian unit. Correct unperturbed dimensions are obtained in the limit of large plate separation. The approximate Gaussian connection between end-to-end distance and free energy of the configurational strand does not allow intolerable crossings of monomers belonging to the "real" subunit. At high concentrations the depletion (adsorption) region tends to become of the order of the subunit dimension. On the other hand, weaker variations of total

concentration extend to the whole interplate region. Coupling between surface effects and long range alterations proves to be important for reliable prediction of surface tension. It is probably also important for an elementary understanding of reversible adsorption. Identification of our model chain with polystyrene is tentative, in the absence of additional information.

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