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Title
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Permalink
https://escholarship.org/uc/item/2hv595qr

Journal
Journal of Chemical Physics, 114(9)

Author
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Publication Date
2000-10-01

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Chemical Sciences Division

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October 2000

Adsorption of Branched Homopolymers on a Solid Surface

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Abstract

Simulation calculations are reported for polymer-wall potentials of mean force and segment-density profiles for homopolymers of different structure as a function of the segment-wall attractive potential.

When there is no attraction between the wall and the polymer segments, the presence of the wall generates a polymer-segment depletion layer whose thickness depends on polymer structure and on surface roughness. Segment-density profiles are characterized by three regions. In the *proximal* region, the segment density is determined by surface roughness and by polymer flexibility. In the *distal* region, the segment density approaches unity asymptotically. In the *central* region, the segment density depends on the correlation length of the polymer in the bulk solution.

When the wall-segment attractive potential is sufficiently large, the depletion layer thickness is reduced and the polymers are adsorbed. When attraction is weak, compact polymers (e.g. dendrimers of high generation) are readily adsorbed. Due to their globular shape, high-generation dendrimers, at weak attractive interactions, are at contact with the surface with numerous segments; globular polymers experience a relatively small entropic penalty for adsorption. By contrast, linear polymers, due to their flexibility at good solvent conditions, pay a high entropic penalty for each segment at contact with the surface. Therefore, at weak attractive interactions, globular polymers are readily adsorbed, whereas linear polymers are more readily adsorbed at stronger attractive interactions.

With rising surface roughness, flexible polymers tend to spread on the surface, whereas branched polymers are repelled at larger distances.

Key Words: polymer adsorption, depletion layer, segment density profile, dendrimer

Introduction

Polymers adsorbed onto solid surfaces are frequently encountered in nature and technology. For example, because selected adsorbed polymer layers influence interparticle potentials, they are widely used to stabilize colloidal suspensions (e.g. paints, coatings, printing inks and ceramic processing).[1] Adsorbed polymers are also used for surface-modification of medical implants;[2, 3] the interfacial behavior of biological macromolecules plays an important role in biomedical applications such as artificial heart valves and joint prostheses.

The behavior of a polymer chain near a surface is determined by many factors.[4] At dilute conditions, solvent quality and polymer-surface interactions are the most important. When polymer-surface interactions are favorable for adsorption, the conformational statistics of polymer chains in the vicinity of the solid surfaces is determined by a competition between the energetic advantage of segmental adsorption and the associated entropic penalty. The entropic penalty arises because adsorption reduces translational freedom and the number of available conformations for the polymer chain.[5]

We report simulations for dilute solutions of homopolymers depleted by, or adsorbed on, a surface. The surface is a layer of hard spheres. The sphere diameter is uniform during one simulation run but is changed in different runs to study the effect of surface roughness. Special attention is given to the effect of polymer branching. In addition to linear polymers,[6] we simulated adsorption of dendrimers up to generation four, 5-arm star polymers, and 5-teeth comb polymers. All polymers are characterized by comparable molecular weight.

To represent dilute good-solvent conditions, polymers are simulated at athermal conditions. Because the solvent is good, entropic penalties due to adsorption are maximized.[4] Because in a poor solvent polymers of different structure are collapsed, adsorption from a good solvent is likely to show more significant differences among polymers characterized by different architectures.

Because different architectures characterize different polymers, we expect different behavior near an impenetrable surface. We find that sorption on a rough surface is enhanced for linear polymers that are more flexible than their branched counterparts. At low attractive interactions, because of their shape, globular polymers (e.g. high-generation

dendrimers) show numerous segments at contact with the surface, and experience a relatively low entropic penalty for adsorption. Thus globular polymers are readily adsorbed on a weakly attractive surface whereas linear polymers, that experience high entropic penalty for adsorption, are not. We also find that at strong attractive interactions, linear polymers spread on the surface and are strongly adsorbed, whereas compact polymers retain their shape and are less favorably adsorbed.

Simulation details

The solvent is represented as a continuum. At good solvent conditions, polymers are modeled as freely-jointed-hard-sphere molecules. Polymer-wall interactions are represented with a square-well potential between each wall sphere and each polymer segment. The potential is given by:

$$\varphi(d) = \begin{cases} \infty & for & d < \frac{1}{2}(\sigma_w + \sigma_p) \\ -\varepsilon & for & \frac{1}{2}(\sigma_w + \sigma_p) \leq d \leq \frac{3}{4}(\sigma_w + \sigma_p) \\ 0 & for & d > \frac{3}{4}(\sigma_w + \sigma_p) \end{cases} \qquad (1)$$

where d is the center-to-center distance between a wall-sphere and a polymer segment, ε is well depth, σ_w and σ_p are the diameters of a wall-sphere and of a polymer-segment, respectively. This simple potential represents a short-distance attractive interaction between the surface and the polymer segments. Its simplicity allows relatively fast calculations, but still retains the essential physics of adsorption. The diameter of a polymer segment, σ_p, is the unit length in all calculations. For simplicity, hereafter σ_p is indicated by σ. The potential between a polymer conformation and the surface is represented by Φ (r), where r is the normal distance of the center of mass of the polymer from the surface. Φ (r) is given by the summation:

$$\Phi(r) = \sum_{i=1}^{N_w} \sum_{j=1}^{N_p} \varphi(d_{ij}) \qquad (2)$$

In Equation (2), N_w is the number of spheres in the wall, N_p is the number of segments in a polymer molecule, d_{ij} is the distance between the ith polymer segment and the jth sphere in the wall. The potential diverges if there is overlap between at least one polymer

segment and one wall sphere. If there are no overlaps, the potential is given by the number of contacts between polymer segments and wall spheres, multiplied by the well depth ε. A polymer segment is 'at contact' with a wall-sphere when the segment-sphere distance is within the well-width of the potential expressed by Equation (1). A polymer segment can be simultaneously 'at contact' with two adjacent wall-spheres.

Equilibrated polymer configurations are generated using the ensemble-growth algorithm.[7] For each polymer architecture, the ensemble is constituted by 20,000 polymers of different configurations. Out of these configurations, 2,000 are randomly chosen and stored for subsequent calculations. Table 1 shows polymer characteristics and calculated sample-average radii of gyration squared. Results shown here are the averages of five different runs.

To compute the polymer-wall potential of mean force, the algorithm proposed by Hall and coworkers[8] was applied with modifications. The program reads from an input file the conformation of a polymer molecule. Then it randomly rotates the polymer configuration and translates it such that the polymer center of mass is at a fixed normal distance r from the wall. Then the wall-polymer potential, $\Phi(r)$, is computed. To improve statistics, the polymer is randomly rotated many times, and the wall-polymer potential is computed for each new orientation of the polymer molecule. Each polymer configuration is rotated at least 1,000 times. Calculations end when all 2,000 polymer configurations have been used. Calculations are repeated for each batch of polymer configurations stored.

The potential of mean force is computed following Hall and coworkers,[8] by

$$\frac{W(r)}{k_B \cdot T} = -\ln \frac{\sum_{l=1}^{M} \Phi_l(r)}{M} \quad , \tag{3}$$

where M is the total number of polymer configurations used to compute the average, Φ_l is the interaction potential between polymer conformation l and the surface. From the potential of mean force, the distribution function,[9] $g(r)$, is computed by:

$$g(r) = \exp\left(\frac{-W(r)}{k_B \cdot T}\right) \quad . \tag{4}$$

4

Polymer-wall interactions are completely defined by the potential of mean force, calculated at different normal distances between the wall and the center of mass of the polymer. However, currently available experimental techniques to study interfacial phenomena are based either on segment density profiles near the surface (e.g. small angle neutron scattering), or on the fraction of polymer segments at contact with the surface (e.g. electron paramagnetic resonance).[10] This work reports several segment-density profiles near the surface.

To compute segment-density profiles as a function of normal distance from the wall, we used a program analogous to the one used to compute the potential of mean force. The polymer configurations are placed at 50 different normal distances r between the polymer's center of mass and the surface, up to a maximum distance of 6.5 times the square root of the polymer's sample-average radius of gyration squared. The segment-density profile is calculated at each r. Then, the mean segment density profile is obtained from a Boltzmann average of the segment densities calculated at each r. The Boltzmann weight is determined by the potential of mean force at each r. The maximum separation was chosen to obtain the segment density in the bulk solution, where interactions with the surface are negligible.

Due the discrete number of distances r used to compute segment-density profiles, the results reported are only semi-quantitative. However, they provide evidence of different homopolymer-adsorption characteristics due to branching.

Results and discussion

a) Depletion Layer

Figure 1 shows the mean segment-density profiles obtained for polymers of different architectures near a non-attractive surface. Different surface roughness was considered. Figure 1a shows results when the diameter of a wall-sphere is half the diameter of a polymer segment. Figure 1b shows results when the diameter of a wall-sphere equals the diameter of a polymer segment, and Figure 1c shows results when the diameter of a wall-sphere is twice the diameter of a polymer segment. The higher the diameter of the wall-sphere, compared to the polymer-segment diameter, the rougher the surface. In Figure 1, the mean segment density $\theta(z)$, calculated at a normal distance z from

the surface, is divided by the segment density in the bulk solution, θ *(bulk)*. For all polymer architectures and for all surface conditions, the surface generates a polymer-segment depletion layer at small distances from the wall. Our results show that the more globular the polymer, the thinner the depletion layer becomes, because of the longer correlation length that characterizes linear coils.

The mean segment-density profile as a function of z presents three characteristic regions. At distances higher than the square root of the polymer's sample-average radius of gyration squared in the bulk solution (*distal region*), the mean segment-density profile approaches unity asymptotically.

At short distances from the surface (*proximal region*), the mean segment-density profile is a function of the surface roughness and of polymer flexibility. Figure 1 shows that when z is less than about twice the polymer-segment diameter σ, the mean segment-density profile is higher for a flexible (linear) polymer than it is for a globular polymer such as a dendrimer of high generation. This difference occurs because a flexible polymer can adjust itself to the surface characteristics more easily than a branched polymer. However, at very short distances from the surface, the mean segment-density profile is the same for all polymer architectures simulated, and depends only on surface characteristics, as indicated in the explosion plots in Figure 1.

At intermediate distances from the surface (*central region*), the mean segment-density profiles are functions of the correlation lengths of the polymers in the bulk solution. Segment density profiles shown here are readily fitted with the equation

$$\frac{\theta(z)}{\theta(bulk)} = \left(\frac{z-D}{\xi}\right)^{m} ,$$

(5)

where D, a function of the surface roughness, provides a measure of the minimum normal distance at which polymer segments are allowed. In this work, D is set half the sum of the wall-sphere and polymer-segment diameters. ξ is the correlation length in the bulk, and m is an empirical exponent.[11] For all cases, our best fits for m and ξ show that both parameters, shown in Table 2, are linear functions of the polymer radius of gyration and do not depend significantly on surface roughness. Figure 2 shows the dependence of m and ξ on the square root of the sample-average radius of gyration squared. Our results show that m increases and ξ decreases with decreasing radius of gyration. ξ is always

higher than the square root of the sample-average radius of gyration squared, and m is always smaller than 5/3. This latter value was computed by de Gennes[11] to describe the segment-density profile near a repulsive wall for linear-polymer solutions. Our values for m for linear polymer are near unity for each surface characteristic studied. The clear dependence of both parameters on the polymer's radius of gyration shows that the mean segment-density profiles, in the central region, are determined by the correlation lengths of the polymers in the bulk solution.

The mean depletion-layer thickness,[12] δ, is computed from

$$\delta = \int_0^\infty \left(1 - \frac{\theta(z)}{\theta(bulk)}\right) dz \quad . \tag{6}$$

At large distances from the surface, the integrand function equals zero. Quantity δ is positive when a depletion layer is observed, whereas it is negative (polymer adsorption) when the mean segment-density profile near the surface is higher than that in the bulk. Table 2 shows our results for the mean depletion-layer thickness for a non-attractive surface, $\delta_{\varepsilon=0}$. For a given polymer, δ increases with rising surface roughness. For given surface characteristics, δ generally falls with decreasing polymer radius of gyration. Our results show that the mean depletion-layer thickness for a generation-three dendrimer is about 25% smaller than that for linear polymer with comparable molecular weight.

b) Polymer Adsorption

Figure 3 shows the distribution function, $g(r)$, as a function of the normal distance between the center of mass of the polymer and the surface. Results are obtained for different segment-surface attractive well depths ε [see Equation (1)]. All results in these plots are for a wall-sphere diameter equal to that for a polymer segment.

At segment-surface well-depth zero, we can see a depletion layer. For all polymers, $g(r)$ equals zero at normal distances r smaller than four times polymer-segment diameter σ.

Increasing the segment-surface attraction, $g(r)$ at given r increases, because the polymers are attracted to the surface. For well-depth equal to -0.10 $k_B T$, the attraction is stronger for the generation-three dendrimer at small distances, while it is stronger for

linear polymer, characterized by longer correlation length, at large distances. For all polymers considered, $g(r)$ equals zero at normal distances smaller than $3\ \sigma$.

For well-depth equal to -0.20 k_BT, for generation-three dendrimer, $g(r)$ has a maximum higher than unity at normal distance of about $7\ \sigma$. At these distances, the probability to find the center of mass of the polymer is greater than that in the bulk solution. The other polymers do not show a maximum in $g(r)$, even though all polymers are clearly attracted to the surface. These results show that a compact structure, like the one that characterizes dendrimers of high generations, enhances polymer adsorption on a smooth, attractive surface.

For well-depth equal to -0.25 k_BT, generation-3 dendrimer, 5-arm star, and comb polymers present a maximum in $g(r)$ larger than unity. The maximum is pronounced for generation-3 dendrimer, whereas for the other polymers it is not significant. The linear polymer does not show a maximum in $g(r)$ at this attractive surface-polymer segment interaction. Our results also show that the probability to find the center of mass of each polymer at normal distance r equal to about $3\ \sigma$ is higher than zero. At these small normal distances from the surface, our results indicate that a flexible polymer can come closer to the surface than a globular polymer.

The accuracy of the results is somewhat worse for stronger attractive potentials. Nevertheless, the results shown here give semiquantitative information concerning the influence of polymer architecture upon polymer adsorption.

For well-depth equal to -0.30 k_BT, all polymers show a maximum in $g(r)$ of about 1.8 at $r \approx 6 \cdot \sigma$. At higher distances, $g(r)$ for linear polymer, characterized by a longer correlation length, is higher than $g(r)$ for branched polymers. At distances smaller than 3σ, our results show that the center of mass of a flexible polymer is allowed to be closer to the surface than the center of mass of a branched, globular polymer.

For well-depth equal to -0.35 k_BT, linear polymers are more strongly adsorbed on the surface, compared to globular polymers. Even though the uncertainty in these results is significant, values for $g(r)$ for linear polymers are always larger than those for generation-3 dendrimers of comparable molecular weight. These results suggest that the work necessary to separate an adsorbed polymer from the surface is higher for linear than for branched polymers. Also, the polymer layer deposited on a surface is thicker for linear

polymers than for branched polymers, in particular for dendrimers of high generation. These latter observations agree with experimental measurements of film thickness for arborescent polystyrenes deposited on mica. Sheiko et al. (1997) reported an increasing ratio of film thickness to hydrodynamic diameter with increasing branch density for arborescent polymers of different generation. A flexible, lightly branched polymer spreads over the surface more than a highly branched, globular polymer.

Figure 4 shows the segment-density profile, $\theta(z)/\theta(bulk)$, as a function of z when $\varepsilon = -0.25$ $k_B T$ and the diameter of a wall sphere is equal to that of a polymer segment. At distances in excess of 5 σ, the mean segment-density profiles are controlled by correlation lengths in the bulk solution. At fixed z, the segment density is higher for globular polymers than for linear chains. However, at distances below 5 σ, the mean segment-density profiles are governed by polymer flexibility. Our results show that, close to the surface, the mean segment density is higher for flexible linear polymers.

The critical attractive well-depth can be defined as the well-depth at which the mean segment-density profile near the surface equals the segment-density profile in the bulk solution. At these conditions, the depletion layer thickness, δ, Equation (6), equals zero. The mean depletion-layer thickness, corresponding to a well-depth of -0.25 $k_B T$, $\delta_{\varepsilon=-0.25}$, is reported in Table 2. For each polymer architecture, the mean depletion-layer thickness computed at $\varepsilon = -0.25$ $k_B T$ is about 40% lower than that at ε equal zero. Because the mean depletion-layer thickness for generation-3 dendrimer is small, about 20% smaller than that for linear polymer, for this polymer architecture, $\varepsilon = -0.25$ $k_B T$ is close to the critical attractive well-depth. For a linear polymer, the absolute value of the critical well-depth is somewhat larger.

Figure 5 compares the distribution function g(r) for polymers of different structure when the surface roughness changes. In all cases, $\varepsilon = -0.25$ $k_B T$. Wall-sphere diameter is either equal to, or twice, the polymer segment diameter. For linear polymers at close distances from the surface (Figure 5a), $g(r)$ does not decrease significantly with rising wall-sphere diameter, because flexible polymers adjust on the surface. For all other polymer structures, $g(r)$ decreases significantly with rising surface roughness, because branched polymers cannot easily spread over the surface.

For all polymers, *g(r)* increases with rising surface roughness at larger distances from the surface. Because the surface-segment potential is characterized by well-width equal to half the sum of wall-sphere and polymer-segment radii, this result is due to the longer range of attractive interactions in the case of larger wall-sphere diameter, compared to the case of smaller wall-sphere diameter. For generation-3 dendrimer, Figure 5d, the increase in *g(r)* at about 7σ is significant, indicating strong adsorption.

Conclusions

Computer simulation calculations are reported for segment-density profiles and potentials of mean force for homopolymers of different structure as a function of the normal distance of the center of mass from a rigid surface. The attraction of the surface, a layer of hard spheres, is characterized by the depth of an attractive square well.

When the surface is non-attractive, a polymer-segment depletion layer is observed close to the surface. For each polymer structure, the mean segment-density profile is characterized by three regions: in the proximal region, because short correlation lengths dominate, segment density profile is determined by surface characteristics and by polymer flexibility. In the distal region, mean segment-density profiles reach unity asymptotically. In the central region, because the correlation length in the bulk solution determines the equilibrium behavior, the mean segment-density profiles depend on the polymer's radius of gyration in the bulk solution.

When the surface-polymer segment potential is sufficiently attractive, polymers are adsorbed. Our results show that compact polymers such as dendrimers of high generation are readily adsorbed at weak attractive interactions. Because the entropic penalty for adsorption is larger for a linear polymer than that for a globular polymer, stronger attractions are required to adsorb a linear polymer. However, at strong attractive interactions, because flexible polymers can spread over the surface, they are adsorbed more strongly than globular polymers.

When surface roughness rises, our results show that the polymers are more strongly attracted at large distances from the surface. However, at close distances from the surface, flexible polymers spread on the surface, whereas branched polymers are repelled.

Acknowledgments

Table 1 Total number of segments, N_p, sample-average radius of gyration squared, $<R_g^2>$, and brief description for each polymer considered in this work. All dendrimers have nodes with functionality equal to two. All polymer segments, nodes, and core have the same size.

Polymer	N_p	$<R_g^2>$ *	description
Linear	100	57±1.2	Linear chain
5-arm star	101	27.4±0.5	Five 20-segment arms connected to the core
Comb	100	35.9±0.8	Four 10-segment teeth on a 60-segment backbone
Gen-1 dendrimer	97	41.2±0.6	16-segment branches
Gen-2 dendrimer	99	31.3±0.5	7-segment branches
Gen-3 dendrimer	91	18.8±0.4	3-segment branches
Gen-4 dendrimer	125	17.9±0.6	2-segment branches

* normalized by polymer-segment diameter σ.

Table 2 Parameters for segment-density-profiles. ξ and m for Equation (4); mean depletion-layer thickness δ corresponding to different surface characteristics. Mean depletion-layer thickness, δ, is for the non-attractive surfaces, $\delta_{\varepsilon=-0}$, and also for attractive surfaces $\varepsilon = -0.25\ k_BT$, $\delta_{\varepsilon=-0.25}$. Results are for different wall-sphere diameters, σ_w; ξ and δ are normalized by polymer-segment diameter σ; m is dimensionless.

Polymer	$\sigma_w=0.5\sigma$			$\sigma_w=1.0\sigma$				$\sigma_w=2.0\sigma$		
	ξ	m	$\delta_{\varepsilon=0.00}$	ξ	m	$\delta_{\varepsilon=0.00}$	$\delta_{\varepsilon=-0.25}$	ξ	m	$\delta_{\varepsilon=0.00}$
linear	12.0	1.10	8.11	12.3	1.06	8.29	4.89	12.2	1.04	8.67
5-arm star	10.3	1.32	6.97	10.2	1.32	7.16	4.54	10.1	1.29	7.53
comb	10.5	1.26	7.27	10.9	1.18	7.47	4.66	10.6	1.18	7.83
Gen-1 dendrimer	-	-	-	11.0	1.16	7.65	-	-	-	-
Gen-2 dendrimer	-	-	-	10.0	1.28	7.18	-	-	-	-
Gen-3 dendrimer	8.0	1.41	5.80	8.0	1.38	6.01	3.94	7.9	1.35	6.38
Gen-4 dendrimer	-	-	-	8.1	1.44	6.06	-	-	-	-

References and notes

1. P.C. Hiemenz, R. Rajagopalan, Principles of Colloid and Surface Chemistry, M. Dekker, Inc., New Yrok, 3rd Ed., 1987.

2. I. Norde in Surface and Interfacial Aspects of Biomedical Applications, Ed. J.D. Andrade, Plenum Press, 1995.

3. J. Wei et al., in From Clone to Clinics, Eds. D.J.A. Crommelin, H. Schellekens, Kluver Academics, 1990.

4. For a review about aspects of polymer absorption, see, for example, A.K. Chakraborty, M. Tirrell, MRS Bull. 21, 28, 1996.

5. L.J. Flory, Principles of Polymer Chemistry, Cornell University Press, Ithaca and London, 1953.

6. Examples of molecular-simulation calculations for the adsorption of linear polymers on flat surfaces are: D. Bratko, A.K. Chakraborty, E.I. Shakhnovich, Computational and Theoretical Polym. Sc. 8, 113, 1998; G.M. Foo, R.B. Pandey, J. Chem. Phys. 107, 10260, 1997; T.C. Clancy, S.E. Webber, Macromolecules 26, 626, 1993; R.H.C. Janssen, E. Mies, P. Cifra, Langmuir 13, 2784, 1997.

7. The non-dynamic ensemble-growth algorithm is efficient for simulating branched polymers or copolymers. See, for example: P.Q. Higgs, H. Orland, J. Chem. Phys. 95, 4506, 1991; D. Bratko, A.K. Chakraborty, E.I. Shakhnovich, Phys. Rev. Letters 76, 1844, 1996 and J. Chem. Phys. 106, 1264, 1997.

8. J. Dautenhahn, C.K. Hall, Macromolecules 27, 5399, 1994.

9. D. Chandler, Introduction to Modern Statistical Mechanics, Oxford University Press, Inc., New York, 1987.

10. See, for example, D.C.J. Lumber, I.D. Robb, I.D. Soutar, L. Swanson, Uysokomolekulyarnye Soed. Ser. A & Ser. B 38, 56, 1996.

11. P.G. de Gennes, Macromolecules 14, 1637, 1991.

12. J.J. de Pablo, H.C. Ottinger, Y. Rabin, AIChE J. 38, 273, 1992.

Figure Captions

Fig. 1 Mean segment-density profiles, $\theta(z) / \theta(bulk)$, for different polymer structures as a function of the normal distance z from the surface. Lines 1 stand for linear polymers, 2 for generation-1 dendrimers, 3 for comb polymers, 4 for generation-2 dendrimers, 5 for 5-arm star polymers, 6 for generation-3 dendrimers, and 7 for generation-4 dendrimers. Figure 1a for a wall-sphere diameter equal to 0.5 σ, Figure 1b for wall-sphere diameter equal to σ, and Figure 1c for wall-sphere diameter equal to 2 σ. The dotted lines in Figure 1c indicate, for linear polymers, the three regions (proximal, central, and distal) that characterize the mean segment-density profile. Explosion pictures show details of the proximal regions.

Fig. 2 Fitting parameters ξ and m for Equation (4) as a function of the square root of the sample-average radius of gyration squared for all mean segment-density profiles; m is dimensionless, while ξ is normalized by σ. Squares are for m, diamonds are for ξ. Lines are guides for the eye.

Fig. 3 Distribution function, $g(r)$, as a function of the center-of-mass normal distance to the surface at different surface-segment attractive potentials ε. Wall-sphere diameter is equal to the polymer segment diameter σ. Lines are guides to the eye. For $\varepsilon = 0$, -0.10, -0.20, and -0.25 k_BT, symbols are larger than uncertainty. For $\varepsilon = $ -0.30 and -0.35 k_BT, the uncertainty is somewhat larger; for clarity, only some error bars are shown. Different symbols represent different polymer structures. Diamonds for linear polymers, full squares for comb polymers, full triangles for 5-arm star polymers, empty triangles for generation-1 dendrimers, empty circles for generation-2 dendrimers, full circles for generation-3 dendrimers, and empty squares for generation-4 dendrimers.

Fig. 4 Mean segment-density profile, $\theta(z) / \theta(bulk)$, as a function of z when ε=-0.25 k_BT and the wall-sphere diameter equals σ. Different lines represent different polymer structures. Line **1** for linear polymers, line **3** for comb polymers, line **5** for 5-arm star polymers, and line **6** for generation-3 dendrimer. The region close to the surface is shown in the exploded inside diagram.

Fig. 5 Distribution function g(r) as a function of r for ε=-0.25 k_BT. Empty symbols are for wall-sphere diameter equal to σ, full symbols are for wall-sphere diameter equal to 2

σ. Figure 5a for linear polymers, Figure 5b for comb polymers, Figure 5c for 5-arm star polymers, and Figure 5d for generation-3 dendrimers.
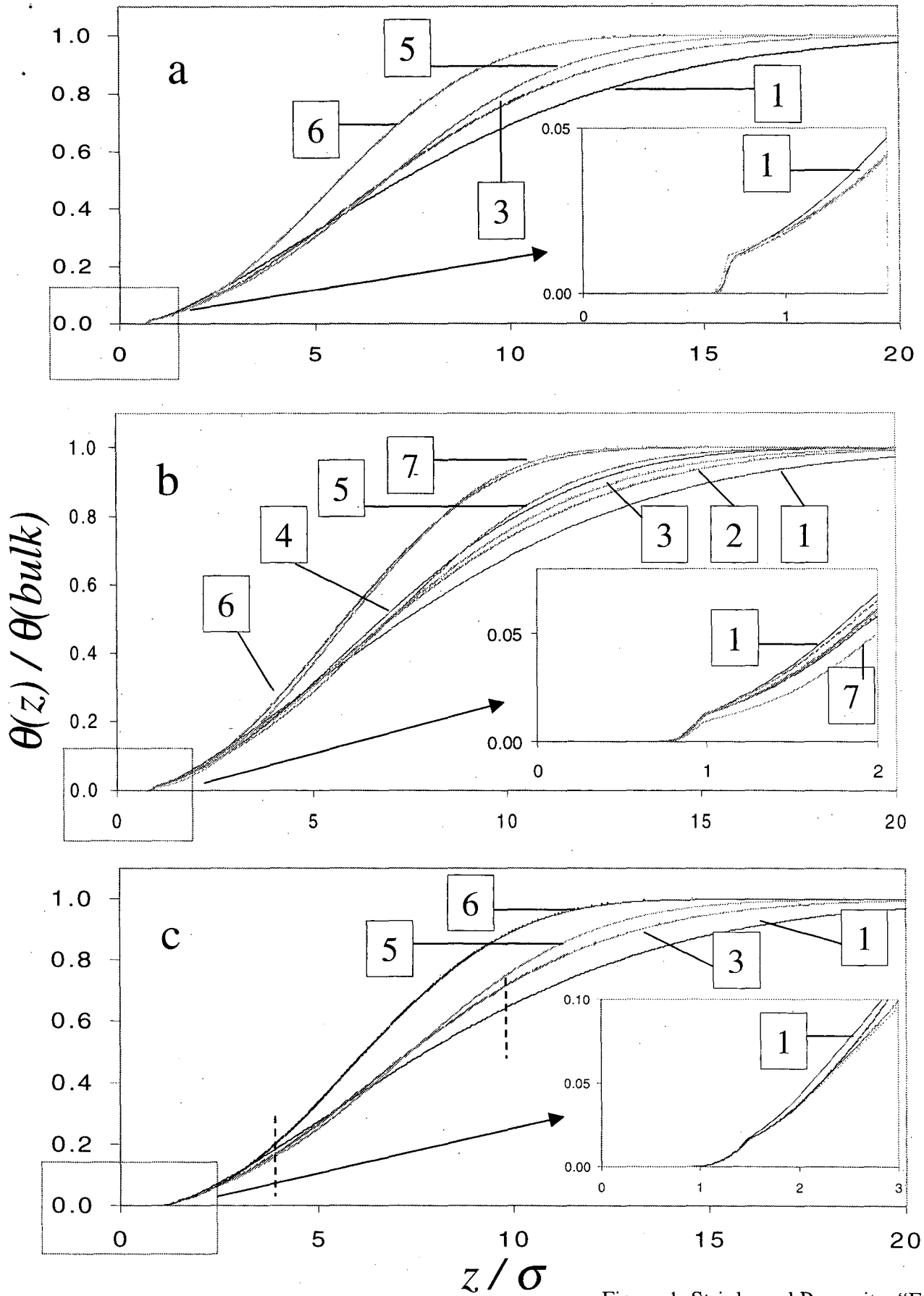
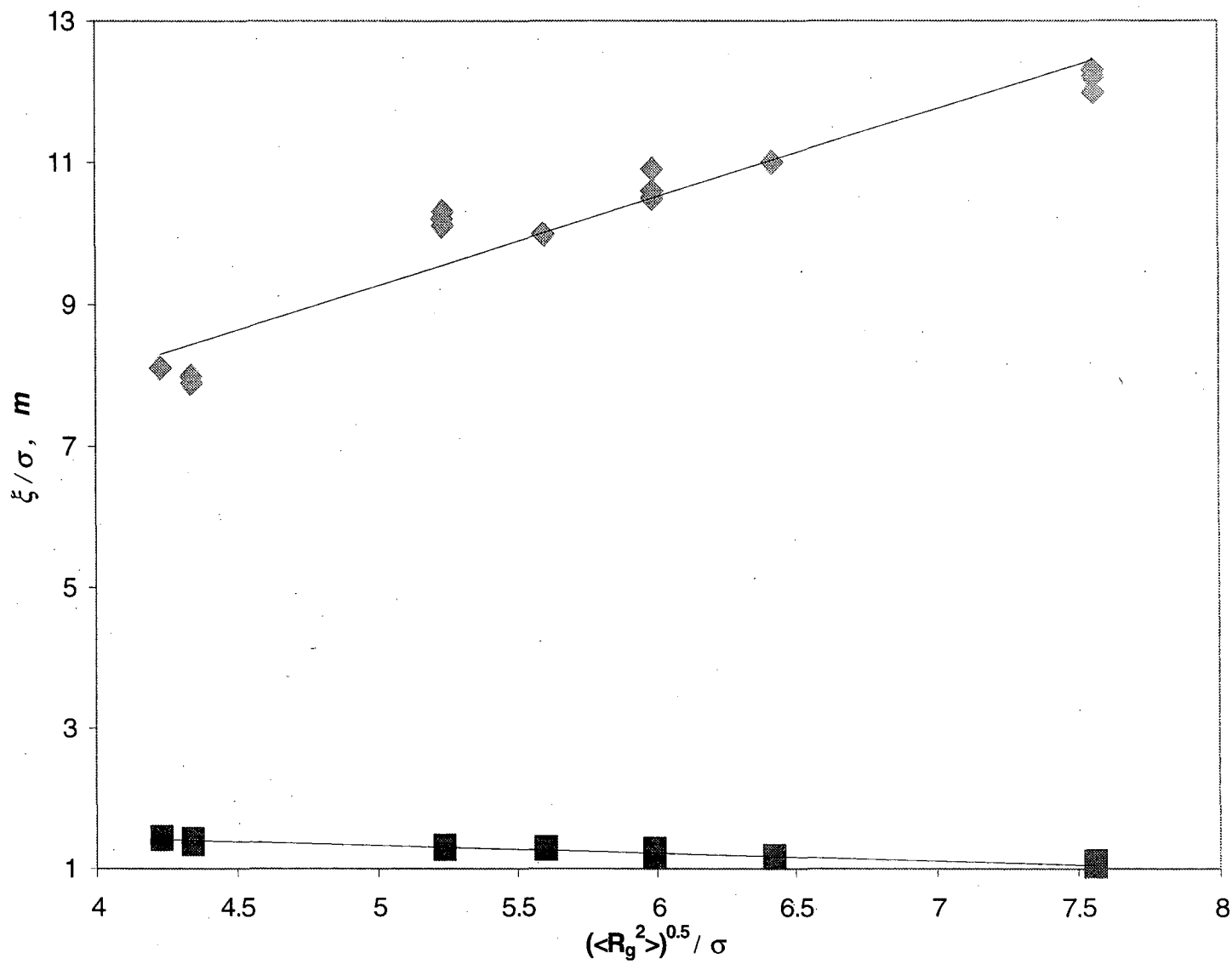Figure 1, Striolo and Prausnitz, "Effect .."

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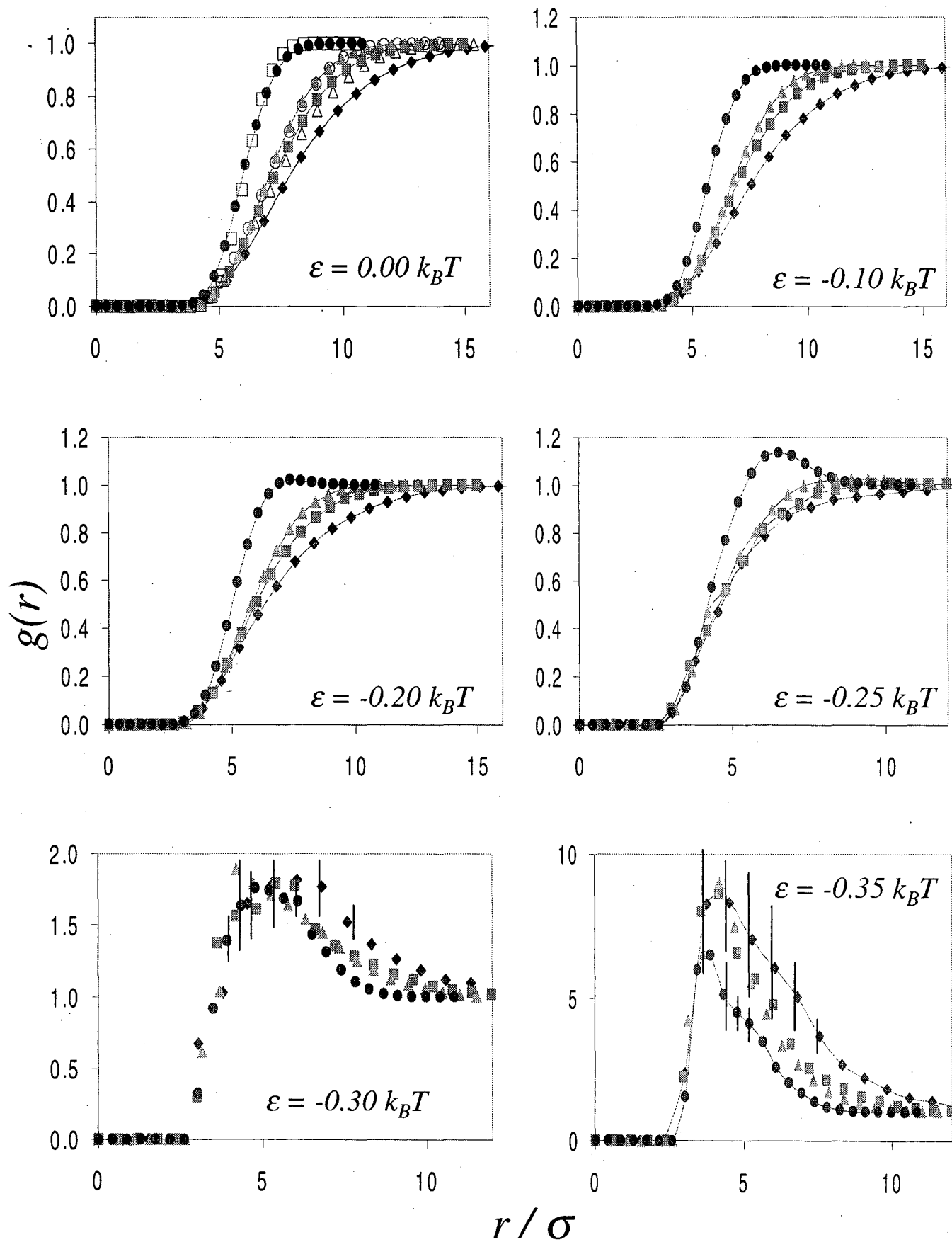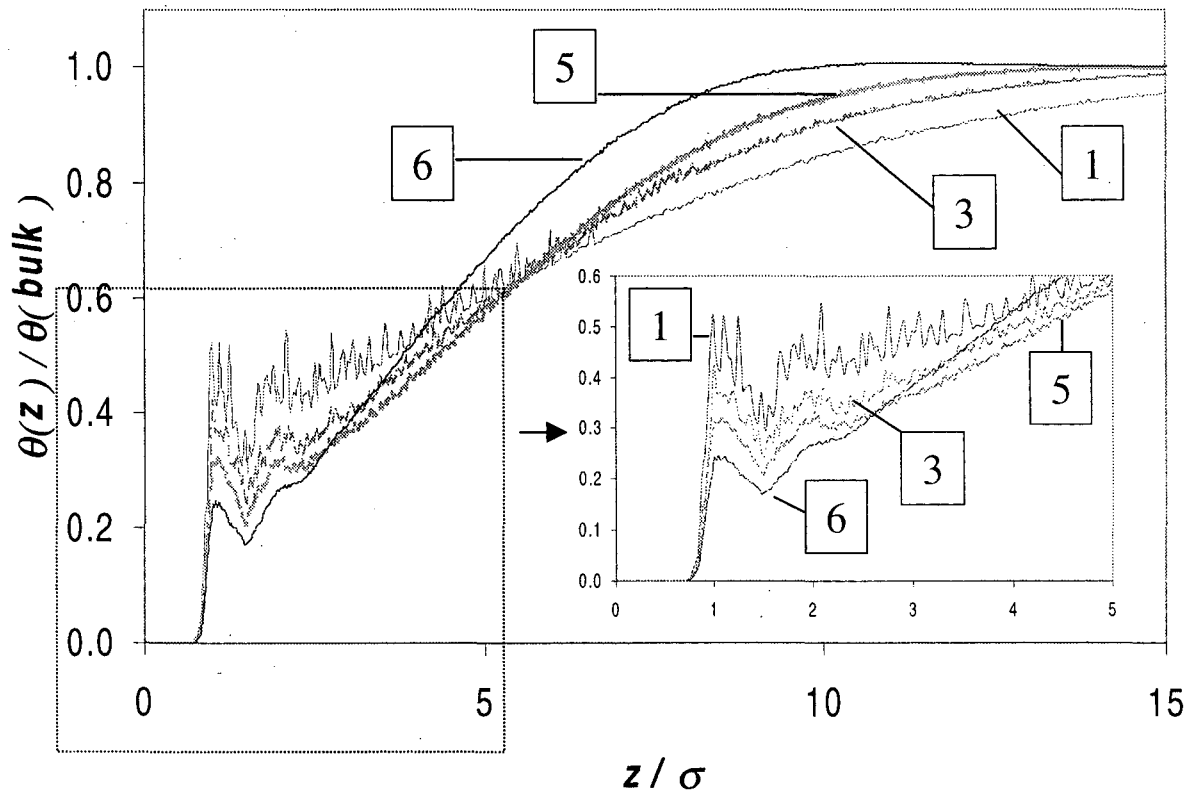Figure 2, Striolo and Prausnitz, "Effect ..."

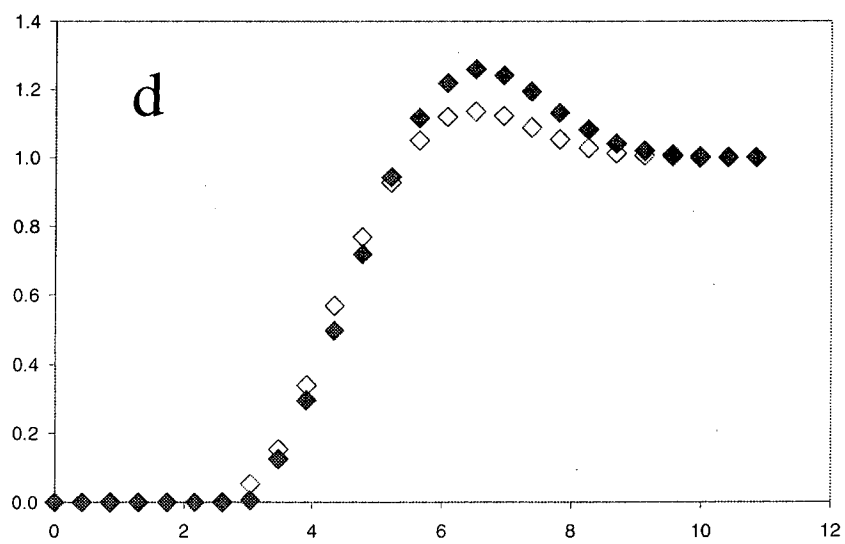Figure 3, Striolo and Prausnitz, "Effect…"
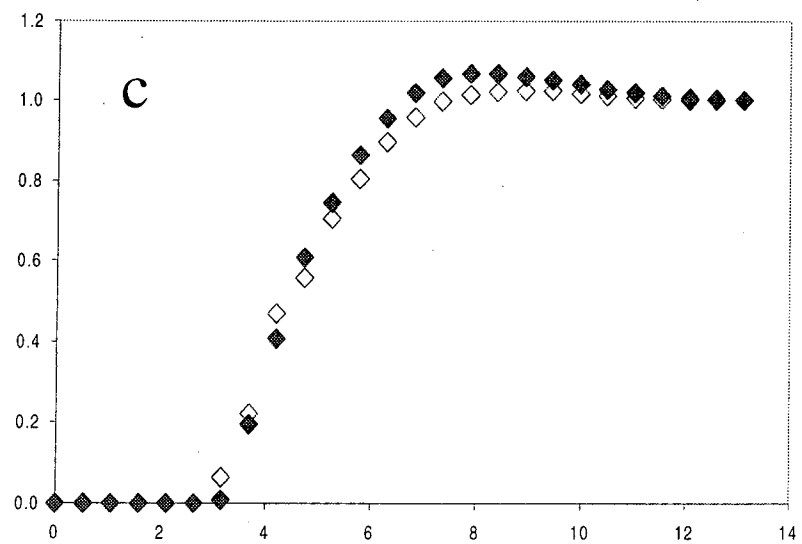
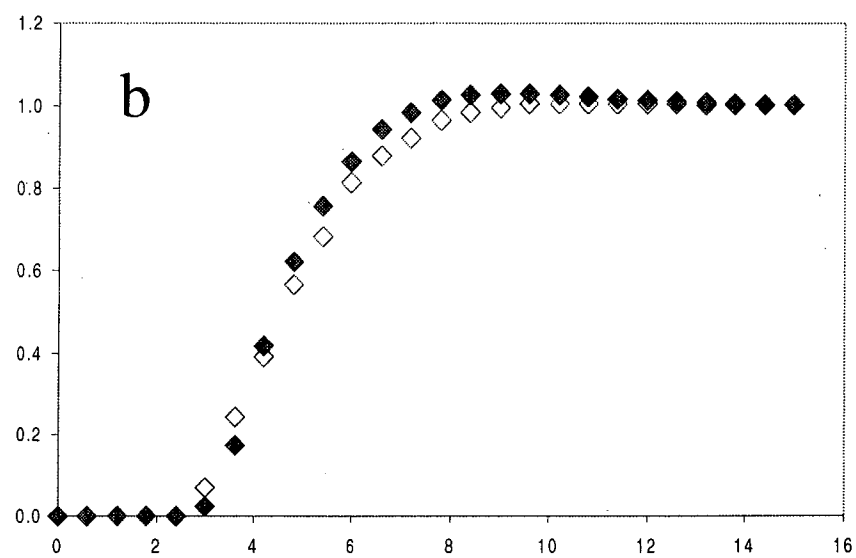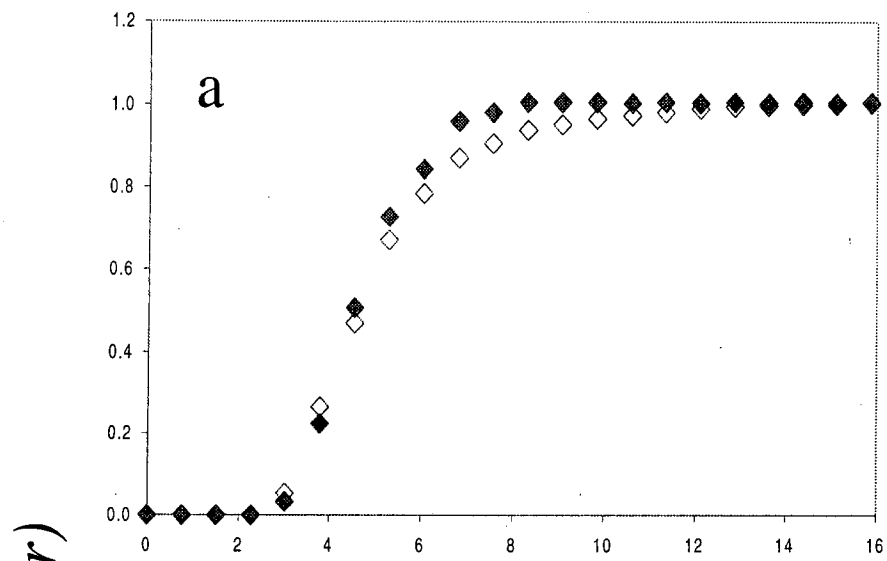Figure 4, Striolo and Prausnitz, "Effect .."

Figure 5, Striolo and Prausnitz, "Effect ..."

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