Structure of confined alkane liquids

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Polymer integral equation theory is employed to calculate structural properties of undecane and short polymer liquids confined between parallel plates. A strong dependence is found on the strength of fluid–surface interactions which is consistent with solvation force measurements using both strongly attractive mica and weakly repulsive hydrocarbon surfaces.

Alkane and polymer fluids near surfaces and in confined geometries are presently of intense interest but poorly understood.[1–3] Direct experimental probing of confined liquid structure is difficult and indirect due to the small amount of material present. Computer simulations on coarse-grained[4] and atomistic[5] model chain molecule fluids have provided considerable insight, but are expensive and limited with regards to accessible time scales, molecular size, and ability to compute the small solvation forces characteristic of the confinement distances of common experimental interest. The goal of this communication is to present, to the best of our knowledge, the first theoretical study of a chemically realistic model of n-alkane and polymer liquids confined between parallel plates of variable adsorptive strength. Comparison is made to experiments using both high and low energy surfaces.

The basis of calculation is the "wall-PRISM" integral equation theory of Yethiraj and Hall[6] for chain molecule fluids confined between flat walls or "slit pores." The reader is referred elsewhere for the technical aspects.[6,7] Briefly, the approach entails applying the bulk polymer RISM (reference interaction site model[8]) theory of Curro and Schweizer[9] in conjunction with the growing adsorbent procedure and its extension to slit pores by Zhou and Stell.[10] Comparisons of the predictions of this theory with simulations of fluids composed of short tangent hard core chains have shown that wall-PRISM is quite accurate.[6] We adopt a hard core interaction between the united atom carbon sites (diameter d) of the C_NH_{2N+2} chains and the site–site Percus–Yevick closure approximation for the bulk PRISM integral equation.[8,9]

There are two noteworthy technical aspects of this work. (1) A chemically realistic description of hydrocarbon molecules, the rotational isomeric state (RIS) model,[11] is employed.[12] This enters the theory via the single chain intramolecular structure factor in the bulk liquid.[6,9] We employ the accurate method of McCoy et al.[13] to calculate this function for n-alkanes using standard RIS parameters. (2) A pair decomposable interaction potential, $u_w(z)$, between the alkane carbon sites and the flat surface is introduced via the closure approximation for the fluid–wall direct correlation function, $C_w(z)$, where z denotes the perpendicular distance of a carbon site from a wall. The site–wall Percus–Yevick closure approximation is employed: $C_w(z) \simeq [1 - \exp(\beta u_w(z))] \, g_w(z)$ for z inside the pore, where $g_w(z)$ is the carbon site–wall pair correlation

function, temperature $T = 1/(k\beta)$, and k is Boltzmann's constant. For a slit pore $z = 0$ or H corresponds to the position of a site's center when at its closest distance of $d/2$ from a wall. The wall–fluid interaction potential consists of a hard core part which defines a total slit width, $W \equiv H + d$, plus a "9–3 tail" in the pore. The latter potential is characterized by a *finite* spatial range, pd, and a strength parameter ϵ which defines the potential upon contact of a carbon site with the wall:

$$u_w(z) = \phi(z) + \phi(H - z), \quad 0 < z < H,$$

$$\phi(z) \equiv \{\epsilon + c\epsilon[\{1 + (z/\sigma)\}^{-9} - \{1 + (z/\sigma)\}^{-3}]\}$$

$$\times \Theta_+(pd - z), \tag{1}$$

where $\Theta_+(y) = 1$ for $y > 0$, $c = 3^{3/2}/2$ and $\sigma = pd/(3^{1/6} - 1)$. The 9–3 form follows from considering the fundamental interactions to be 12–6 Lennard-Jones and integrating over the three-dimensional (continuum) solid whose surface constitutes a pore wall. Since the bulk fluid is chosen to be athermal, ϵ represents the *relative* energy difference between fluid–fluid and fluid–wall contacts and thus is a direct measure of the energetic driving force for physical adsorption. This simple potential model has been constructed in the spirit of representing the competition between fluid–fluid and fluid–surface contacts in terms of a single surface–fluid interaction parameter.

Numerical solutions of the bulk PRISM[9] and wall-PRISM[6] integral equations are obtained using a standard Picard iteration method. The site–wall pair correlation function defines a one-body inhomogeneous density profile, $\rho(z) = \rho_b g_w(z)$, where ρ_b is the bulk site number density. We also define a coarse-grained density of the nth layer from the surface as

$$\rho_1 = z_1^{-1} \int_0^{z_1} dz \, \rho(z),$$

$$\rho_n \equiv (z_n - z_{n-1})^{-1} \int_{z_{n-1}}^{z_n} dz \, \rho(z) \quad \text{for } n \geqslant 2, \tag{2}$$

where z_n is the location of the nth minimum from the wall of $\rho(z)$. This definition coincides with the natural layering embodied in the oscillatory features of the calculated density profiles. A density-weighted "adsorption energy" per unit area is introduced as $E_{ADS} \equiv \int_0^{pd} u_w(z) \rho(z)$. The pressure in our slit pore is given by[14]
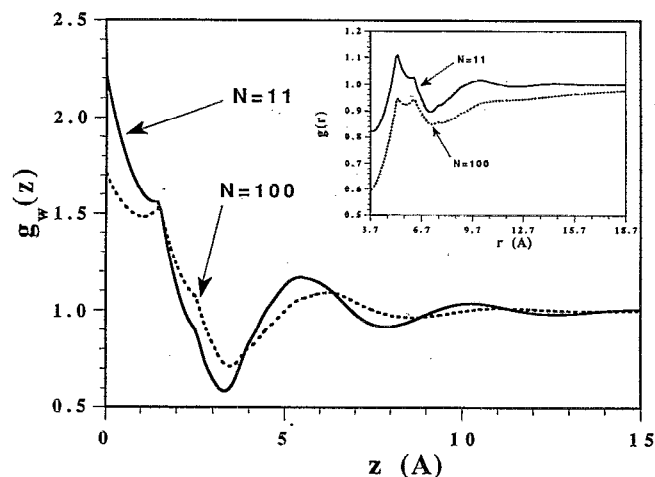
FIG. 1. Normalized carbon center density profile for undecane ($N=11$) and a short polymer ($N=100$) at an isolated *neutral* surface plotted as a function of distance (in angstroms) from the surface minus $d/2$. The inset shows the bulk intermolecular site-site pair correlation function.
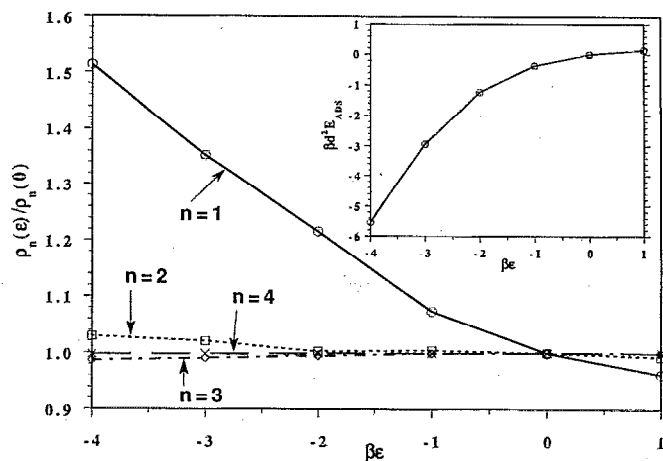

FIG. 2. Average density of layer n for undecane liquid *relative* to the neutral surface case as a function of fluid–surface interaction strength. The inset shows the density-weighted adsorption energy in dimensionless form.

$$\beta P(H) = \rho(z=0) - \beta \int_0^{H/2} dz \frac{d\phi(z)}{dz} \rho(z). \qquad (3)$$

The solvation pressure, or force per unit area, is $P_{\mathrm{SOLV}}(H) = P(H) - P(H \to \infty)$.[15] In many experiments the confining surfaces consist of orthogonally crossed cylinders each of large radius of curvature R. The measured force may then be related to the solvation pressure of the parallel plate system within the Derjaguin approximation[15]:

$$\frac{F(H)}{2\pi R} = \int_H^\infty dH' \, P_{\mathrm{SOLV}}(H') \equiv w(H), \qquad (4)$$

where $w(H)$ represents the work per unit area to bring the parallel plates from infinity to the separation H.

As a first, experimentally motivated application of the theory we have considered n-undecane ($N=11$) at $T=298$ K. The effective hard core diameter of a methylene group is $d=3.73$ Å,[16] and the experimental $\rho_b=0.031\,35$ Å^{-3}. The spatial range of the surface-fluid potential tail is taken to be $0.25d$. The normalized density profile for a neutral wall ($\epsilon=0$) in the single surface limit ($H \to \infty$) is shown in Fig. 1. As previously found by Yethiraj *et al.*,[12] significant oscillatory structure, indicative of layering of chain segments parallel to the surface, extends 12–15 Å. This layering occurs even though the bulk chain-averaged site–site intermolecular pair correlation function, $g(r)$, exhibits only weak solvation shell structure. The enhancement of the maximum $\rho(z)$ by a factor of roughly two relative to its bulk analog is very similar to the hard sphere fluid,[17] even though the absolute magnitudes are roughly 5 times larger for the latter. Strong enhancement of the structure of the density profile occurs with larger fluid–surface attractive potentials.[7]

Results for a $N=100$ "polymer" under *identical* conditions (d, T, ρ_b) as undecane are also shown in Fig. 1. The bulk $g(r)$ exhibits "negative" correlation for all intersite separations ($h(r) = g(r) - 1 < 0$) and a long-range tail or

"correlation hole".[9,18] Although the density profile in the pore is similar to that of undecane, structural features are less pronounced.

The coarse-grained layer densities *relative to their values for the neutral surface case* in the "single wall" limit ($H \to \infty$) are plotted in Fig. 2. Explicit results for the *neutral* surface for $N=11$ (and 100; not plotted) chains are given by: $\rho_n/\rho_b = 1.32(1.27)$, $0.99(0.98)$ for $n=1,2$ and unity for $n>3$. The first layer densifications are significantly smaller than the 60%–80% enhancements found from simulations of the hard sphere fluid.[17] A general pattern of behavior emerges for all cases studied: a strong density enhancement in the first layer, followed by nearly bulk behavior in all sucessive layers. The local densification due to surface-fluid attraction might lead to a significant slowing down of dynamical processes of the monomers in the first layer. Such a phenomenon has been observed or inferred experimentally[1-3,19,20] and in some recent computer simulations.[4,5] A related experimental phenomenon is that for short polymer liquids confined between strongly attractive mica surfaces the force profiles display a repulsive component (of order the radius-of-gyration, R_g)[19] suggestive of an effective "tethering" of polymer chains at the surface and hence an immobilized layer of thickness R_g. Distinct theoretical ideas concerning the origin of this force have been proposed[21,22] based on the common premise that an effective vitrification of the near surface layer results in a partially *non*equilibrium situation. On the other hand, for neutral surfaces this phenomenon is not experimentally observed, possibly due to the theoretically predicted much lower near surface density. A dimensionless "adsorption energy" is presented in the inset of Fig. 2. The strong increase of this quantity with surface–fluid attraction is expected to have important implications for desorption kinetics.[20]

The solvation pressure of undecane liquid is shown in Fig. 3 for a range of $\beta\epsilon$ values and plate separations, W, of common experimental interest. These damped, oscillatory
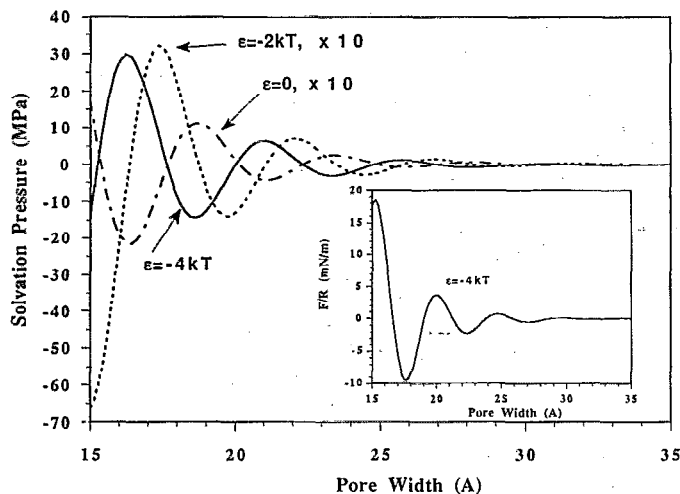
FIG. 3. Solvation pressure (in megapascals) for undecane liquid confined between flat parallel plates separated by a fixed pore width for several values of the fluid–surface interaction strength. Note the scale change introduced for $\beta\epsilon=0$ and -2. The inset shows the solvation force (in millinewtons per meter) computed using the Derjaguin approximation.
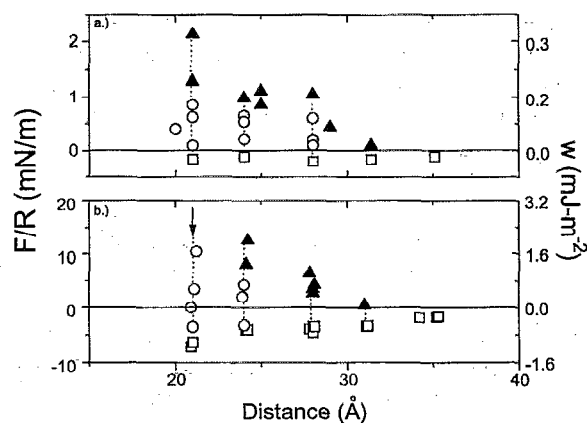
FIG. 4. Experimental solvation force data for undecane on (a) mica and (b) OTE. The left ordinate shows force, normalized by the mean radius of curvature of the crossed cylinders, plotted against undecane film thickness. The right ordinate shows the equivalent energy per unit area between parallel plates. Triangles(circles) indicate points measured upon squeezing(pulling) the plates together(apart). Squares indicate the force at which plates jump apart. The dotted lines connect the corresponding repulsive and attractive minima. The arrow indicates that data points under squeezing conditions were measured at higher force at this separation.

pressure profiles can be empirically represented by the simple form

$$P_{\mathrm{SOLV}}(W) \simeq A \cos\left(\frac{2\pi[W+\Delta]}{D}\right)\exp(-W/\xi), \qquad (5)$$

where the phase adjustment Δ is a few angstroms. The period of the oscillations, D, is 4.7 ± 0.1 Å for all values of the surface–fluid interaction. This is considerably larger than the hard core CH_2 group diameter ($d=3.73$ Å) but is nearly identical to the space-filling *thickness* of a sequence of three consecutive methylene units (or four consecutive methylene groups in the all-*trans* conformation) of $\simeq4.6$ Å. However, D does increase for longer chains; for example, $D\simeq5.4$ Å for a $N=100$ fluid under identical conditions as undecane. The extrema of the force profiles systematically shift inwards with increasing (decreasing) attractive fluid–surface interaction (degree of polymerization). The decay length of the envelope of the oscillatory profile is in the range $\xi=3.00$–3.15 Å. Perhaps the most interesting feature in Fig. 3 is the strong dependence of the amplitude of the force profile on surface-fluid interaction. An enhancement of roughly 30 occurs when the neutral surface is made strongly attractive, and in general the amplitude is a weakly decreasing function of N.[7] For $\beta\epsilon\leqslant-1$ the A parameter (in megapascals) in Eq. (5) is well fit for undecane by: $A=461.3+37.38\exp(-5\beta\epsilon/4)$. Finally, an example of the solvation force calculated using the experimentally relevant Derjaguin approximation is presented in the inset of Fig. 3. The relative change of the amplitude with $\beta\epsilon$ is similar to the flat plate case.[7]

The influence of the spatial range parameter p of Eq. (1) was also explored. As an example, if the spatial range is doubled ($p=1/2$) but the integrated strength $\int dz\,\phi(z)$ of the surface–fluid interaction is held constant by decreasing $|\epsilon|$ appropriately, then there is virtually no change in the solvation force profile. Comparisons of the theory with

molecular dynamics simulations of short alkanes and detailed studies of the influences of density, wall–fluid potential and single molecule structure on equilibrium properties will be reported elsewhere.[7]

To test these issues experimentally, force-distance profiles of undecane confined between solid surfaces were obtained using methods described previously.[23] To create a surface whose interaction with undecane is neutral or weakly repulsive ($\beta\epsilon\geqslant0$), the strongly attractive mica surface was coated with a methyl-terminated monolayer of condensed octadecyltriethoxysilane (OTE).[24] The surface energy of OTE is roughly 21 mJ/m², much less than the mica value of 200–400 mJ/m² (Ref. 24). Using the latter number as an estimate of the cohesive energy of mica, the known[5] Lennard-Jones energy parameter for methylene groups of roughly 60 K, a standard geometric combining law, and a typical solid density, one estimates the net energy lowering for transferring a methylene group from the bulk liquid to contact with a (continuum) mica surface to be in the range of 900–1500 K. Hence, for undecane between mica a rough estimate of the effective $\beta\epsilon$ parameter at room temperature is in the range of 3–5.

The experimental results are shown in Fig. 4 and illustrate several important points. First, both force profiles are oscillatory, although well-known experimental instabilities[15] preclude measuring the force profile curve at all plate separations. The period roughly equals 4–5 Å consistent with the theory and previous measurements of confined alkanes.[2,15,25] The positions of the minima shift with ϵ, in qualitative agreement with Fig. 3. Second, the force oscillations are at film thicknesses in the range of 20–40 Å, a region where the solvation energy is small relative to kT and hence difficult to determine from computer simulations. The asymmetry of the measured oscillations may reflect surface deformations.[25] Third, the magnitudes of the

attractive minima are roughly an order of magnitude smaller for undecane between OTE as against bare mica, in agreement with the theoretical expectations discussed above. Finally, the strong sensitivity of our theoretical results to ϵ suggests a unifying perspective from which to interpret the puzzling experimental fact that force profiles measured by different groups on supposedly the same systems can be so variable with regards to amplitudes of extrema, film thickness at extrema, and number of oscillations observed. Prior speculations include moisture effects,[25] rogue contamination,[26] or variability in relative crystallographic orientation of the opposed mica lattices.[27] All these effects can be viewed as variations of the effective surface energy of the solid against the confined fluid, and thus can be understood as changes of an effective wall-fluid interaction strength ϵ.

ACKNOWLEDGMENTS

[1] J. N. Israelachvili and P. M. McGuiggan, Science **241**, 795 (1988).

[2] M. L. Gee and J. N. Israelachvili, J. Chem. Soc. Faraday Trans. **86**, 4049 (1990).

[3] S. Granick, Science **253**, 1374 (1991).

[4] K. F. Mansfield and D. N. Theodorou, Macromolecules **22**, 3143 (1989); I. Bitsanis and G. Hadziioannou, J. Chem. Phys. **92**, 3287 (1990); A. Yethiraj and C. K. Hall, J. Chem. Phys. **95**, 1999 (1991); P. Thompson, G. Grest, and M. Robbins, Phys. Rev. Lett. **68**, 3448 (1992); I. Bitsanis and C. Pan, Makromol. Chem. Makro, Symp. **65**, 211 (1993); J. Chem. Phys. **99**, 5520 (1993).

[5] M. Vacatello, D. Y. Yoon, and B. Laskowski, J. Chem. Phys. **93**, 779 (1990); M. W. Ribarsky and U. Landmann, ibid. **97**, 1937 (1992); Y. Wang, K. Hill, and J. G. Harris, J. Phys. Chem. **97**, 9013 (1993); Langmuir **9**, 1983 (1993); M. Vacatello and F. Auriemma, Makromol. Chem. Theory Simul. **2**, 77 (1993); D. Yoon, G. D. Smith, and T. Matsuda, J. Chem. Phys. (to be published).

[6] A. Yethiraj and C. K. Hall, J. Chem. Phys. **95**, 3749 (1991).

[7] K. P. Walley, K. S. Schweizer and A. Yethiraj (in preparation).

[8] D. Chandler, Studies in Statistical Mechanics, edited by E. Montroll and J. Lebowitz (North-Holland, Amsterdam, 1982), Vol. 8, p. 274, and references cited therein.

[9] See, for example, K. S. Schweizer and J. G. Curro, Macromolecules **21**, 3070 and 3082 (1988); K. S. Schweizer and J. G. Curro, Adv. Polym. Sci. (in press).

[10] D. Henderson, F. Abraham, and J. A. Barker, Mol. Phys. **31**, 1291 (1975). Y. Zhou and G. Stell, Mol. Phys. **66**, 767 (1988).

[11] P. J. Flory, Statistical Mechanics of Chain Molecules (Wiley, New York, 1969).

[12] Wall-PRISM theory has been recently applied [A. Yethiraj, J. G. Curro, K. S. Schweizer, and J. D. McCoy, J. Chem. Phys. **98**, 1635 (1993)] to compute the single neutral surface density profiles of n-butane and polyethylene hard core melts using a RIS model.

[13] J. D. McCoy, K. G. Honnell, J. G. Curro, K. S. Schweizer, and J. D. Honeycutt, Macromolecules **25**, 4905 (1992).

[14] Our result is a straightforward extension of prior work on atomic fluids; see, for example, G. Rickayzen, Mol. Phys. **55**, 161 (1985).

[15] J. N. Israelachvili, Intermolecular and Surface Forces (Academic, New York, 1992).

[16] K. G. Honnell, J. D. McCoy, J. G. Curro, K. S. Schweizer, A. H. Narten, and A. Habenshuss, J. Chem. Phys. **94**, 4659 (1991); K. G. Honnell (unpublished).

[17] J. R. Henderson and F. van Swol, Mol. Phys. **51**, 991 (1984).

[18] P. G. deGennes, Scaling Concepts in Polymer Physics (Cornell University, Ithaca, 1979).

[19] J. P. Montfort and G. Hadziioannou, J. Chem. Phys. **88**, 7187 (1988); R. G. Horn and J. N. Israelachvili, Macromolecules **21**, 2836 (1988); R. G. Horn, S. J. Hirtz, G. Hadziioannou, C. W. Frank, and J. M. Catala, J. Chem. Phys. **90**, 6767 (1989); H. W. Hu and S. Granick, Science **258**, 1339 (1992).

[20] H. E. Johnson and S. Granick, Science **255**, 966 (1992).

[21] P. G. DeGennes, C. R. Acad. Sci. Paris **305**, 1181 (1987).

[22] H. W. Hu, S. Granick, and K. S. Schweizer, J. Noncryst. Sol. (in press).

[23] J. N. Israelachvili and G. E. Adams, J. Chem. Soc. Faraday Trans. 1 **74**, 975 (1978); H.-W. Hu and S. Granick, Macromolecules **23**, 613 (1990).

[24] C. Kessel and S. Granick, Langmuir **7**, 532 (1991).

[25] H. K. Christenson, D. Gruen, R. G. Horn, and J. N. Israelachvili, J. Chem. Phys. **87**, 1834 (1987).

[26] J. L. Parker and P. Attard, J. Phys. Chem. **96**, 10 398 (1992); H. K. Christenson and V. V. Yaminsky, Langmuir **9**, 2448 (1993).

[27] P. M. McGuiggan and J. N. Israelachvili, J. Mater. Res. **5**, 2232 (1990).