

The quasitwodimensional regime of fluids absorbed in porous media

Phil Adams, J. R. Henderson, and J. P. R. B. Walton

Citation: *The Journal of Chemical Physics* **91**, 7173 (1989); doi: 10.1063/1.457334

View online: <http://dx.doi.org/10.1063/1.457334>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/91/11?ver=pdfcov>

Published by the AIP Publishing

Articles you may be interested in

[Structural quantities of quasi-two-dimensional fluids](#)

J. Chem. Phys. **140**, 104506 (2014); 10.1063/1.4867284

[Dissipation in quasi-two-dimensional flowing foams](#)

Phys. Fluids **21**, 053102 (2009); 10.1063/1.3142502

[Equilibrium Structure of the QuasiTwoDimensional Dipolar Fluid](#)

AIP Conf. Proc. **661**, 209 (2003); 10.1063/1.1571314

[Vapor–liquid coexistence of quasi-two-dimensional Stockmayer fluids](#)

J. Chem. Phys. **106**, 3311 (1997); 10.1063/1.473079

[Quasitwodimensional dynamics of plasmas and fluids](#)

Chaos **4**, 227 (1994); 10.1063/1.166049



The quasi-two-dimensional regime of fluids absorbed in porous media

Phil Adams and J. R. Henderson^{a)}

School of Chemistry, University of Leeds, Leeds LS2 9JT, United Kingdom

J. P. R. B. Walton

British Petroleum, Sunbury Research Centre, Chertsey Road, Sunbury-on-Thames, Middx TW16 7LN, United Kingdom

(Received 23 June 1989; accepted 18 July 1989)

We investigate the one-body structure of fluids confined within model pores when the confinement is sufficient to force the fluid into a quasi lower-dimensional regime. The concept of the quasi-two-dimensional regime of atomic fluids confined to symmetric planar slit geometry is introduced and statistical mechanical arguments are shown to predict a universal form for the density profile; or to be more precise, to imply that the many-body contribution to the one-body structure is a particular universal function of position. Computer simulation data of Lennard-Jones fluid confined to planar slit pores are presented, which clearly illustrate the statistical mechanical prediction. Generalizations of this phenomenon to include fluid mixtures, molecular fluids and nonplanar geometries are discussed.

I. INTRODUCTION

The theory of fluids confined in model porous media has received much recent attention.^{1-4,6,8,9} Part of this impetus has arisen from the realization that the confining dimension of a pore (L) plays a role analogous to that of the bulk thermodynamic fields temperature (T) and chemical potential (μ) and the surface fields that control the wetting characteristics in the limit of very large pore width.^{2,6} Another aspect has been the availability of computer simulation data for model fluids confined in model pores.^{3,8,9} The most tractable such class of system is the case of atomic fluids confined between a pair of planar walls. Here, one studies a Hamiltonian system of the form

$$H = \sum_i v(z_i) + H_{FF}, \quad (1)$$

where H_{FF} denotes the fluid-fluid interaction Hamiltonian. For a symmetric slit, we have

$$v(z) = \phi(z + L/2) + \phi(L/2 - z), \quad (2)$$

where L is a measure of the pore width and $\phi(z)$ is the external field arising from a single wall located at $z = 0$ [with $\phi(z < 0) = \infty$, $\phi(\infty) = 0$].

One of the many interesting aspects of confined fluid behavior is the transition to low dimensionality at very strong confinement. For example, if the radius of a cylindrical pore is sufficiently small such that any pair of fluid molecules have a very low probability of being able to pass one another, then the fluid can be regarded as a quasi-one-dimensional system. In planar geometry, a quasi-two-dimensional regime arises when the slit width is small enough to force any pair of particles in the act of passing one another to travel at least partly around one another (in the plane parallel to the slit walls). The precise nature of these low-dimensional regimes depends on the choice of ensemble. At fixed number of particles (N), i.e., for closed pores, a true two-

dimensional system is reached in the limit of zero pore width. However, for open pores, which is the usual case of interest, reducing the pore width below an intermolecular diameter will tend to squeeze fluid out of the ends of the pore, i.e., the chemical potential would need to be infinite to yield a nonzero two-dimensional density in the limit of zero pore width. An alternative way of considering extremely narrow open pores is to note that the three-dimensional density, $\rho(\mathbf{r})$, does not become infinite in the limit of zero pore width/diameter; for example, compare with the results calculated for the exactly solvable model of hard rods confined to a line of finite length.⁴ Thus, the pair correlations must become weak-gas-like at the limit of extreme confinement within open pores, i.e., in this limit a finite number of particles per unit volume implies zero number of particles per unit area. A formal statement of this result is provided by the potential distribution theorem⁵:

$$\rho(\mathbf{r}) = \Lambda^{-3} \exp\{[\mu - v(\mathbf{r})]/kT\} \langle \exp\{-\psi(\mathbf{r})/kT\} \rangle, \quad (3)$$

where Λ is the deBroglie wavelength ($\Lambda^2 \equiv h^2/2m\pi kT$) and $\psi(\mathbf{r})$ denotes the instantaneous interaction of a particle (at position \mathbf{r}) with the rest of the fluid. If the center of the pore is used to define the origin, then the extreme confinement regime corresponds to

$$\rho(0) \equiv \Lambda^{-3} \exp\{[\mu - v(0)]/kT\}. \quad (4)$$

The leading-order deviation from this limit is given by a lower-dimensional second virial coefficient.⁶ In this paper we derive a general result for $\rho(z)$ that is applicable throughout the quasi-two-dimensional fluid regime, including situations in which the fluid is dense both as a two-dimensional and as a three-dimensional system.

The natural statistical mechanical description of open systems belonging to the class of Hamiltonians (1) is via the compressibility route, based on the fact that isothermal functional differentiation of the grand potential (Ω) with respect to the one-body field [$v(\mathbf{r}) - \mu$] generates the probability distribution function hierarchy $\rho^{(s)}(1...s)$,

^{a)} Address for correspondence: Dr. J. R. Henderson, School of Chemistry, University of Leeds, Leeds, LS2 9JT, United Kingdom, [PHC6JRH@UK.AC.LEEDS.AI].

$$\delta\Omega/\delta[v(\mathbf{r}) - \mu] = \rho(\mathbf{r}), \quad (5a)$$

$$\delta\rho(1)/\delta[v(2) - \mu] = (-1/kT)\{\delta(12)\rho(1) + \rho^{(2)}(12) - \rho(1)\rho(2)\}, \quad (5b)$$

etc. From Eq. (5) one can write down a variety of important sum rules; for example, note that as well as yielding expressions for $\partial\Omega/\partial\mu$ and $\partial\rho(\mathbf{r})/\partial\mu$, the compressibility route generates analogous sum rules involving derivatives with respect to any of the surface fields arising from $v(\mathbf{r})$ and, in the case of pores, derivatives with respect to the pore width parameter L [cf. Eq. (2)]. The latter case provides a direct link with the phenomenon known as solvation structure.⁶ In this work we focus attention on a particular compressibility route sum rule, obtained by applying Eq. (5b) to the case of an infinitesimal translation of the entire system (including the external field)⁷:

$$\delta v(\mathbf{r}) \sim \nabla v(\mathbf{r}); \quad \delta\rho(\mathbf{r}) \sim \nabla\rho(\mathbf{r}),$$

$$-kT\nabla\rho(1) = \rho(1)\left\{\nabla v(1) + \int d\mathbf{z}\rho(2)h(12)\nabla v(2)\right\}, \quad (6)$$

where $h(12)$ denotes the total correlation function, $h(12) \equiv [\rho^{(2)}(12) - \rho(1)\rho(2)]/\rho(1)\rho(2)$. Some of the consequences of sum rule (6) applied to the case of an atomic fluid confined between a pair of planar hard walls have been discussed previously.⁶ In particular, in the quasi-two-dimensional regime it was found that the density profile reduced to an essentially universal form, which in fact had been previously observed in the special case of hard sphere fluid confined between a pair of planar hard walls.⁸ In Sec. II below, we show that the above mentioned universality of the one-body structure of fluids confined to very narrow slits is not restricted to hard wall boundaries, i.e., it generalizes to include the quasi-two-dimensional regime of every atomic fluid confined between two identical planar walls of arbitrary potential $\phi(z)$, consistent with strong confinement. In Sec. III we give examples of this behavior obtained from computer simulation studies of Lennard-Jones (LJ) fluid confined between planar attractive walls. A final section discusses generalizations of these results on the structure of quasi-two-dimensional fluids, to encompass fluid mixtures, molecular fluids and nonplanar confinement geometries.

II. ATOMIC FLUIDS CONFINED WITHIN PLANAR SLITS

Two illustrative examples of density profiles of atomic fluids in the quasi-two-dimensional regime are sketched in Fig. 1. If plotted separately the two density profiles might appear to be very different. That is, it is important to be clear about how we are defining the positions of the walls. In Fig. 1(a) the slit walls are hard walls situated at $z = \pm L_a/2$, i.e., the centers of the fluid atoms are unable to penetrate the regions $|z| > L_a/2$. In Fig. 1(b) we show an analogous situation when the walls model a more realistic system; namely, $v(z)$ contains soft repulsive and weak attractive terms. In this case the mathematical containing boundaries are much further apart [$v(z) = \infty$ for $|z| > L_b/2$] but the physically relevant containment region is approximately the same as in Fig. 1(a), i.e., $\tilde{L}_b \approx L_a$. Quasi-two-dimensional regimes

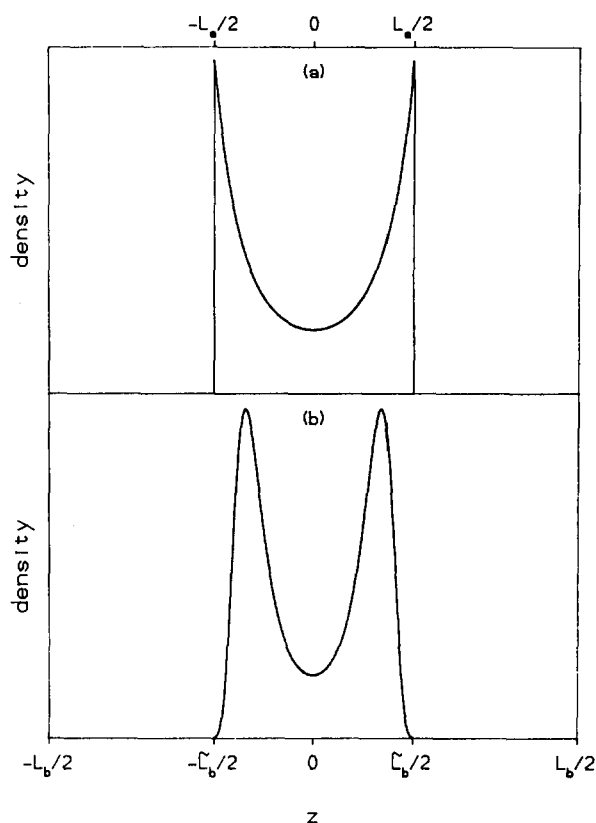


FIG. 1. Schematic density profiles illustrating two classes of fluid structure that can belong to the quasi-two-dimensional regime of atomic fluids; (a) hard wall boundary conditions, (b) a symmetric wall-fluid field possessing soft repulsive and moderately weak attractive contributions. L_a and L_b are the pore widths defined by planes of infinite wall-fluid repulsion, while in (b), \tilde{L}_b denotes an effective pore width.

arise whenever the probability of two atoms possessing identical coordinates in the plane of the walls is sufficiently small. For the system shown in Fig. 1(a), one requires $g(2|z|, -z, z) \ll 1$ for all $|z| < L_a/2$, where $g(r_{12}, z_1, z_2)$ denotes the pair correlation function [$g(12) = h(12) + 1$]. If the fluid was composed of hard spheres of diameter σ , this condition would be uniquely defined by the requirement $L_a < \sigma$. For a general pair-potential $[u(r)]$ fluid confined between a pair of hard walls, a reasonable definition of the quasi-two-dimensional regime would be $L_a < \tilde{\sigma}$ where $\exp\{-u(\tilde{\sigma})/kT\} = 10^{-3}$, say. The above discussion can be carried over to general $v(z)$, by making an appropriate substitution for L_a ; e.g., for the system shown in Fig. 1(b) the quasi-two-dimensional regime would be such that $\tilde{L}_b < \tilde{\sigma}$, since \tilde{L}_b has been chosen as the largest length such that $\rho(z)$ is too small to be of any significance for $z > \tilde{L}_b/2$ (for example, a typical case would be to take \tilde{L}_b such that $\exp\{-v(z > \tilde{L}_b/2)/kT\} < 10^{-2}$). That is, the quasi-two-dimensional regime arises whenever the pair probability $\rho(z)g(2|z|, -z, z)$ is sufficiently small such that it can be treated as zero, for all values of z .

Let us now consider sum rule (6) applied to the quasi-two-dimensional regime as defined above. First, the planar symmetry enables us to reduce Eq. (6) to the form

$$-kT \frac{\partial \ln[n(z_1)]}{\partial z_1} = \int_{-\infty}^{\infty} dz_2 \rho(z_2) h_0(z_1, z_2) v'(z_2), \quad (7)$$

where $n(z)$ denotes the one-body "y" function, i.e.,

$$\rho(z) \equiv n(z) \exp\{-v(z)/kT\} \quad (8a)$$

and we have introduced the notation

$$h_0(z_1, z_2) \equiv 2\pi \int_{|z_2 - z_1|}^{\infty} dr r h(r, z_1, z_2). \quad (8b)$$

Substitution of Eq. (2), as is appropriate to symmetric slits centered on the origin, enables us to rewrite Eq. (7) as

$$-kT \frac{\partial \ln\{n(z_1)\}}{\partial z_1} = \int_{-\infty}^{\infty} dz_2 \rho(z_2) [h_0(z_1, z_2) - h_0(-z_1, z_2)] \phi'(z_2 + L/2), \quad (9)$$

where we have made use of the symmetry of the system:

$$\rho(z) = \rho(-z); \quad h_0(z_1, z_2) = h_0(-z_1, -z_2). \quad (10)$$

Let us now pursue the consequences of the quasi-two-dimensional regime to the form of the solution of Eq. (9). Here, using the notation of Fig. 1(b), we are restricting the discussion to $|z_1| < \tilde{L}/2$, where \tilde{L} is defined such that $\rho(z)$ is small enough for $|z| > \tilde{L}/2$ to enable the integration on the right-hand side of Eq. (9) to be confined to the region $|z_2| < \tilde{L}/2$. That is, the maximum value of $|z_2 - z_1|$ that we need to consider is \tilde{L} . Now consider the square brackets term in the integrand of Eq. (9), which for our purposes is conveniently split up into two terms via the concept of $\tilde{\sigma}$ discussed above (i.e., the quasi-two-dimensional regime is $\tilde{L} < \tilde{\sigma}$):

$$\begin{aligned} &[h_0(z_1, z_2) - h_0(-z_1, z_2)] \\ &= -2\pi \int_{|z_2 - z_1|}^{|z_2 + z_1|} dr r \\ &+ 2\pi \int_{\tilde{\sigma}}^{\infty} dr r [h(r, z_1, z_2) - h(r, -z_1, z_2)], \end{aligned} \quad (11)$$

where in the first term on the right-hand side we have utilized the conditions $|z_2 + z_1|, |z_2 - z_1| < \tilde{L} < \tilde{\sigma}$ together with the fact that $\tilde{\sigma}$ is defined such that when $r < \tilde{\sigma}$ we can replace $h(r, z_1, z_2)$ by its hard-core value: -1 . The significance of the quasi-two-dimensional regime to sum rule (9) arises from the absence of terms in Eq. (11) associated with $|z_2 - z_1| > \tilde{\sigma}$. In particular, the right-hand side of Eq. (11) should be very accurately represented by a simple universal dependence on z_1 :

$$[h_0(z_1, z_2) - h_0(-z_1, z_2)] \rightarrow z_1 f(z_2). \quad (12)$$

The first term on the right-hand side of Eq. (11) is exactly of the form (12); namely, $-4\pi z_1 z_2$. To judge the validity of Eq. (12) in the context of the final term in Eq. (11), it is instructive to consider how one might attempt a direct evaluation of Eq. (11) via some approximate correlation function theory. A standard approach, that clearly involves significant error, would be to replace $g(r_{12}, z_1, z_2)$ by some bulk fluid radial distribution function $g(r)$; here, the last term in Eq. (11) would vanish. Thus, some z dependence of the pair correlation function must be introduced before the final term can contribute at all. One might envisage being able to provide a reasonable theory for the leading-order z dependence; say an approximation for the second term in the expansion

$$\begin{aligned} g(r, z_1, z_2) &= g(r, 0, z_2) + z_1 [\partial g(r, z_1, z_2) / \partial z_1]_{z_1=0} \\ &+ (1/2) z_1^2 [\partial^2 g(r, z_1, z_2) / \partial z_1^2]_{z_1=0} + \text{H.O.T.} \end{aligned} \quad (13)$$

and to expect such a theory to be fairly accurate when applied to an integral equation such as Eq. (9). To go beyond this leading-order term would constitute a remarkably advanced integral equation theory indeed. However, note that even if all three terms explicitly given on the right-hand side of Eq. (13) were known exactly, the final term in Eq. (11) is still exactly of the form (12). Only the higher-order terms labeled H.O.T. in Eq. (13) can lead to deviations from the form (12). Such terms may well contribute if the system solidifies, but for fluid states one can reasonably expect deviations from Eq. (12) to be of no physical significance to sum rule (9). Thus, substituting Eq. (12) into Eq. (9), we are led to propose as a general result

$$n(z) = n(0) \exp\{\alpha z^2\}; \quad |z| < \tilde{L}/2 < \tilde{\sigma}/2 \quad (14a)$$

which when combined with Eq. (8a) gives

$$\rho(z) = \rho(0) \exp\{\alpha z^2 - [v(z) - v(0)]/kT\}; \quad \tilde{L} < \tilde{\sigma}. \quad (14b)$$

That is, in the quasi-two-dimensional regime, the density profiles of atomic fluids confined to symmetric slits consist of a trivial nonuniversal factor $[\exp\{-v(z)/kT\}]$ multiplied by the universal form (14a). Furthermore, this universal form is determined by only two system dependent parameters (functions of T, μ, L and the surface field variables); i.e., $n(0)$ and α . Note that this universality is very general since nowhere have we been required to specify the nature of the fluid-fluid interactions (apart from the restriction to atomic symmetry, but see Sec. IV below) and the wall field $v(z)$ can be any symmetric containing field (2).

III. COMPARISON WITH COMPUTER SIMULATION DATA

If the arguments of Sec. II are correct, then computer simulation studies of model fluids confined to the quasi-two-dimensional regime should not be able to detect deviations from the density profile form (14b). Thus, whenever simulation studies of planar fluid-slit systems enter the regime $\tilde{L} < \tilde{\sigma}$ the form of the resulting density profile is known theoretically. This result will also be of value to real experimental studies, whenever scattering experiments on strongly confined fluids are feasible. In this section we present computer simulation data that illustrate this phenomenon.

Our specific model is of the form (1,2), with $H_{FF} = \sum_{i < j} u(r_{ij})$ and

$$u(r) = \begin{cases} [u_{LJ}(r) - u_{LJ}(r_c)], & r < r_c \\ 0, & r > r_c \end{cases}, \quad (15a)$$

$$u_{LJ}(r) = 4\epsilon_{FF} [(\sigma_{FF}/r)^{12} - (\sigma_{FF}/r)^6], \quad (15b)$$

$$\begin{aligned} \phi(z) &= (4\pi/5) \epsilon_{SF} \sigma_{SF}^2 \rho_S \Delta [(\sigma_{SF}/z)^{10} - 2.5(\sigma_{SF}/z)^4 \\ &- 5\sigma_{SF}^4/6\Delta(z + 0.61\Delta)^3] \end{aligned} \quad (15c)$$

with the following choice of parameters:

$$\begin{aligned} \epsilon_{FF}/k &= 95.2 \text{ K}; \quad \sigma_{FF} = 3.75 \text{ \AA}; \quad r_c = 2.5\sigma_{FF}, \\ \epsilon_{SF}/k &= 51.6 \text{ K}; \quad \sigma_{SF} = 3.57 \text{ \AA}; \quad \rho_S = 0.02 \text{ \AA}^{-3}; \\ \Delta &= 3.35 \text{ \AA}. \end{aligned} \quad (15d)$$

TABLE I. Simulation data.

L^*	$\langle N \rangle^b$	α^c	$\ln\{n^*(0)\}^d$
2.0	83.4	9.18 ± 0.35	-3.561 ± 0.008
2.1	83.9	9.55 ± 0.23	-3.525 ± 0.007
2.2	84.8	10.60 ± 0.14	-3.467 ± 0.006
2.3	88.2	12.86 ± 0.08	-3.493 ± 0.005
2.4	97.5	17.57 ± 0.08	-3.790 ± 0.006

^a L^* is the pore width in units of σ_{FF} ; see Eqs. (2) and (15).

^b $\langle N \rangle$ denotes the average occupancy of a simulation box.

^c α is the slope of a plot of $\ln\{n^*(z^*)\}$ vs z^{*2} , obtained from GCMC simulation data [see Fig. 2(b)]. The errors denote one standard deviation from a simple least-squares fit to the above mentioned plot. To avoid unwanted bias from data belonging to the extreme tails of the density profile (where the percentage statistical error is very high) we ignored all simulation points corresponding to $\rho^* < 0.02$. (Note, the quoted errors correspond to the specific values of $\langle N \rangle$ listed in column b. Different sets of runs would yield different values of $\langle N \rangle$ and hence alter the entries in columns c and d; in the worst cases this effect would correspond to increasing the given error estimates by a factor of three. The values of α are particularly sensitive to $\langle N \rangle$ at very small L , since a large change in α is required to significantly affect the density profile of a strongly confined fluid.)

^d $\ln\{n^*(0)\}$ denotes the intercept of the plot used to obtain α .

This form of the wall potential arose because we wished to make use of a grand canonical Monte Carlo (GCMC) simulation program developed by Walton and Quirke.⁹ Reference 9 was specifically interested in modeling nitrogen confined between planar graphite walls. For this case, ρ_s was taken as 0.114 \AA^{-3} , which constitutes a very strong wall-fluid attractive field. In fact, at normal bulk liquid temperatures this choice of ρ_s led to the density being strictly zero over a region encompassing the middle of the pore, in place of profiles of the type shown in Fig. 1(b). In this situation, we observed that although (14) was a reasonable description clear deviation could be observed, as would be expected from our argument based on (13) if solidification had occurred. Accordingly, to allow the presence of fluid throughout the pore we altered the value of ρ_s to that given in Eq. (15d), which is typical of van der Waals solid-fluid interactions used by previous workers.¹³

Defining the reduced variables

$$z^* = z/\sigma_{FF}; \quad \rho^*(z^*) = \rho(z/\sigma_{FF})\sigma_{FF}^3; \quad L^* = L/\sigma_{FF}, \\ T^* = kT/\epsilon_{FF}; \quad \mu^* = \mu^{ex}/\epsilon_{FF} + T^* \ln\{\rho^*\}, \quad (16)$$

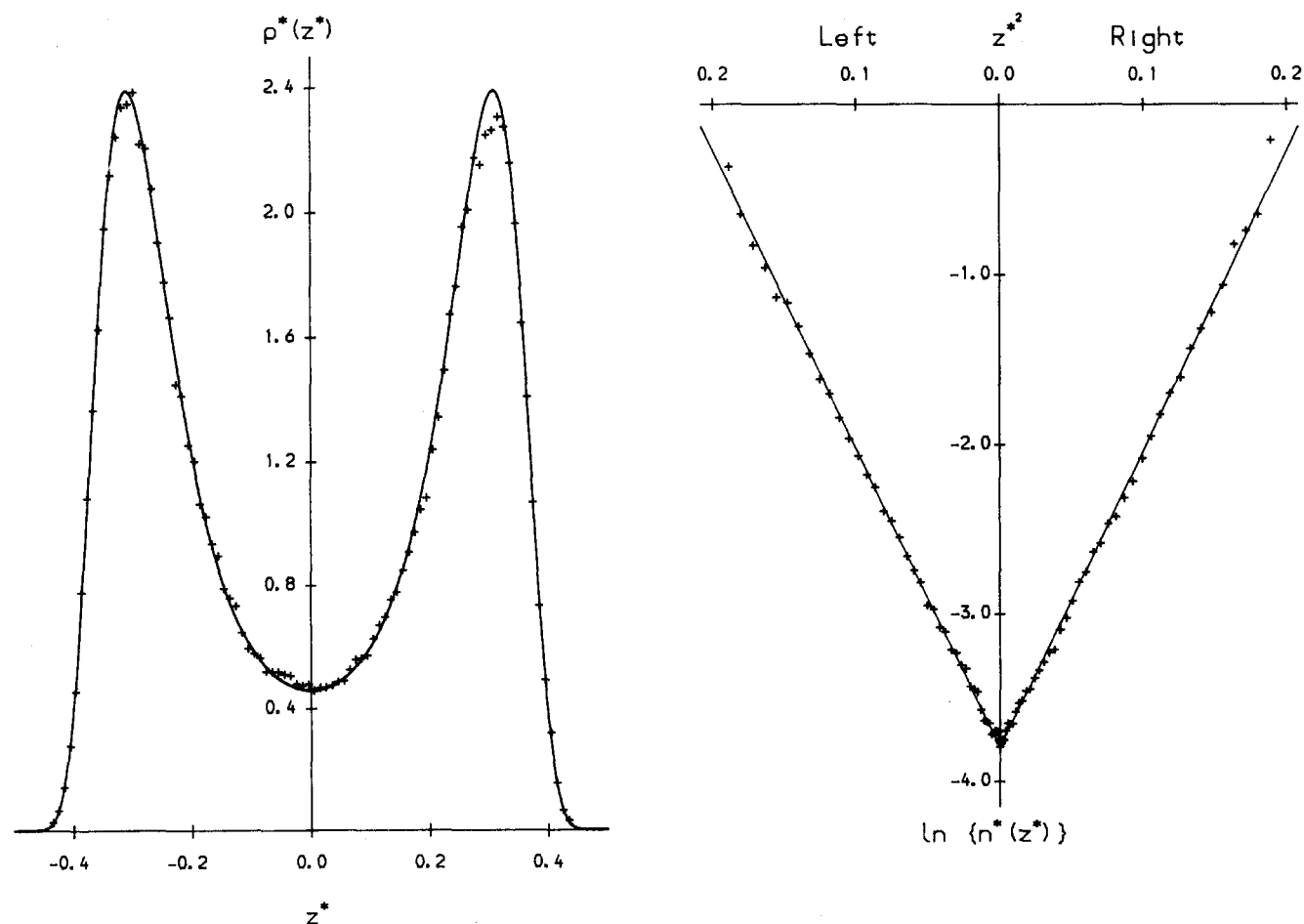


FIG. 2. (a) Density profile of LJ fluid confined to a symmetric pore of width $L^* = 2.4$; see Eqs. (2) and (15). The symbols denote GCMC simulation data collected over 10^6 simulation steps. The curve shows the profile obtained from a fit to the universal form (14). (b) The profile data of (a) plotted in the form $\ln\{n^*(z^*)\}$ versus z^{*2} . The left-hand and right-hand sides of the system are displayed separately. The straight lines show a simple least-squares fit to the expected form (14a), assuming a symmetric profile; see also Table I caption.

where μ^{ex} denotes the excess chemical potential, we chose to vary L^* across the quasi-two-dimensional regime at fixed $(T^*, \mu^*) = (0.8, 0.0)$. This relatively high value of μ^* was chosen to counteract the effect of fluid being squeezed out of the pore; i.e., it ensured a sufficiently high density inside the pore. The boundary conditions orthogonal to the walls were periodic and the overall dimensions of the simulation box were taken to be $L \times 10\sigma_{FF} \times 10\sigma_{FF}$. Under these conditions we obtained average occupancies $\langle N \rangle$ in the range 80 to 100 particles. A single GCMC step consisted of one attempted particle translation, ten attempted particle insertions and ten attempted particle deletions.⁹ Each system was equilibrated from an empty pore for 10^5 steps and statistical averages were collected over 10^6 steps. For our choice of parameters the quasi-two-dimensional criterion $\tilde{L} < \tilde{\sigma}$, discussed in Sec. II above, is $\tilde{L} < 0.91\sigma_{FF}$. This required us to take $L^* < 2.5$, to ensure that we remained inside the quasi-two-dimensional regime.

Figure 2(a) shows the measured density profile in our widest pore; $L^* = 2.4$. The symbols denote simulation data while the curve shows a fit to the form (14). The status of the universal form (14a) can be judged from Fig. 2(b), where we plot $\ln\{n(z)\sigma_{FF}^3\}$ versus z^{*2} which is expected to yield a straight line. There is clearly no observable deviation from the predicted form (14a), within the statistical error of our simulation procedure. The line through the data points is a least-squares fit to a straight line; slope α , intercept $\ln\{n(0)\sigma_{FF}^3\}$. Although we have plotted data from both sides of the pore separately, the fit assumes a symmetric profile. The values of α and $n^*(0)$ obtained from Fig. 2(b) were used to plot the full curve in Fig. 2(a). Note that because of the validity of the universal form (14a) the simulation experiment is only measuring two quantities, α and $n^*(0)$; i.e., the curve in Fig. 2(a) is a measured profile obtained from combining all the simulation data in the manner of Fig. 2(b). So, at any chosen value of z the profile is known to a much greater accuracy than is suggested by some of the individual data points plotted in Fig. 2(a).

The procedures used to generate Figs. 2(a) and 2(b) were repeated at four smaller values of L . Although the density profile structure changed dramatically across this range, there was no qualitative change in the behavior of $n(z)$. In particular, the universal form (14a) remained valid [in the manner of Fig. 2(b)] in all cases, within simulation error. In one case $L^* = 2.1$, the largest source of simulation error arose from a slight asymmetry in the profile that had not been fully removed after 10^5 steps. In fact, MC procedures are sometimes prone to yielding nonsymmetric profiles in confined symmetric geometries; however, Eq. (2) does not allow this to correspond to a true equilibrium average. In Table I, we list our results obtained from straight line fits to the form (14). In Figs. 3–6 we show the measured density profiles; i.e., direct data together with smoothed data obtained from (14). As the two walls are placed closer together, the profiles change from a double peak structure to a single peak, via a flat top profile. However, all the profiles belong to the quasi-two-dimensional regime. The strong changes in density distribution arise from the competition between the wall-fluid forces and the fluid-fluid repulsive

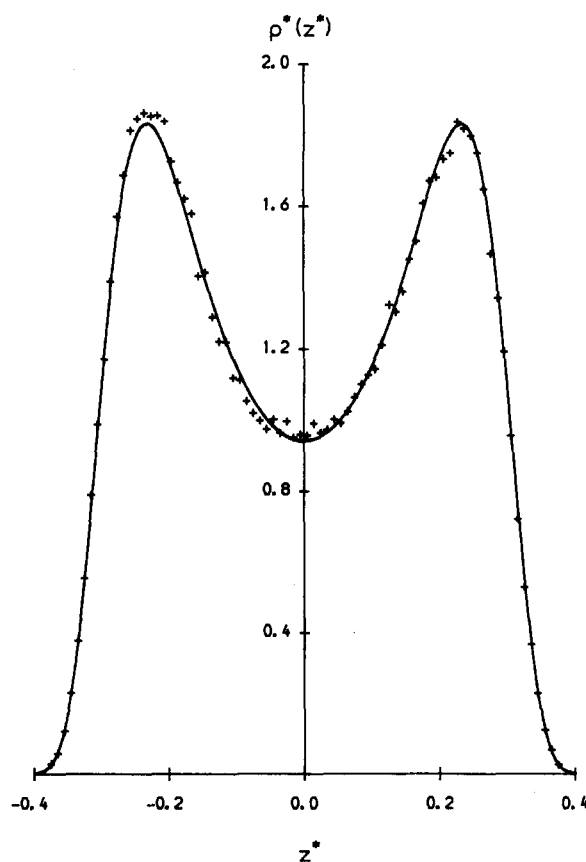


FIG. 3. $L^* = 2.3$; see caption to Fig. 2(a).

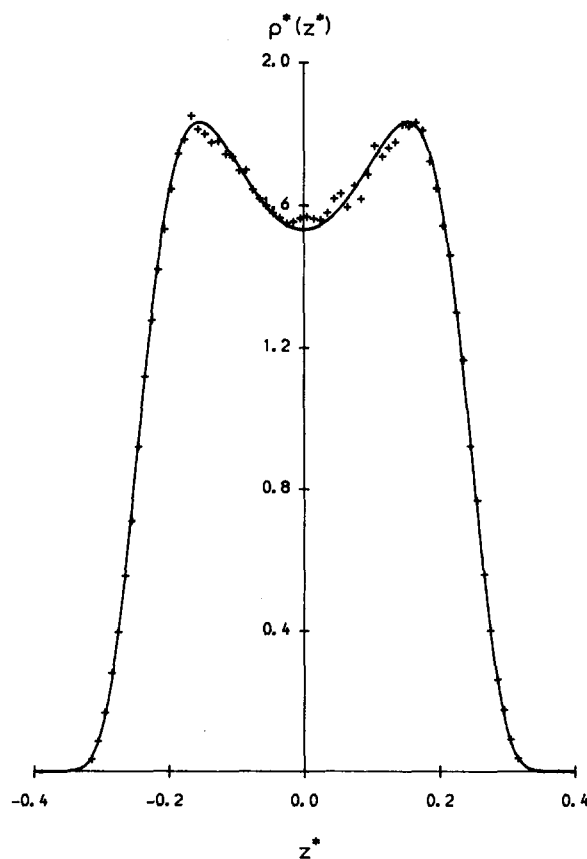
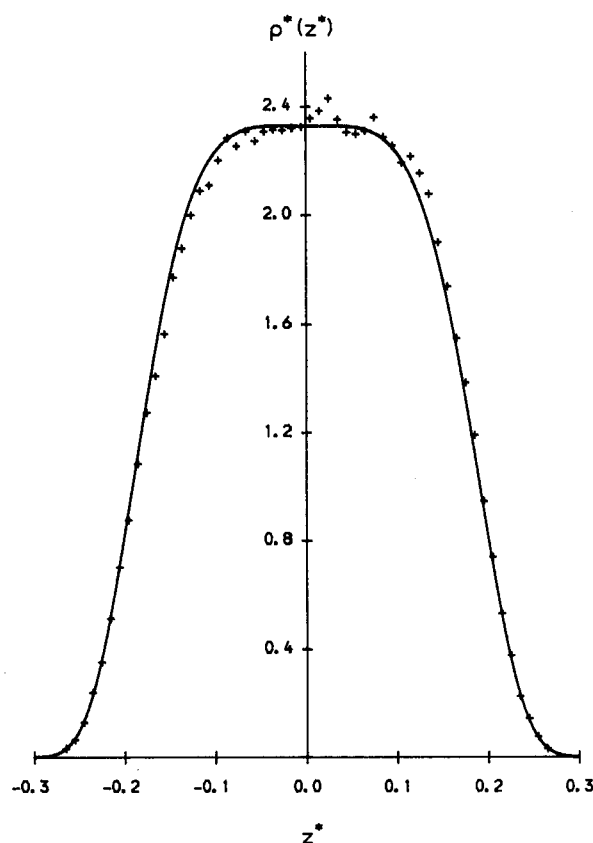
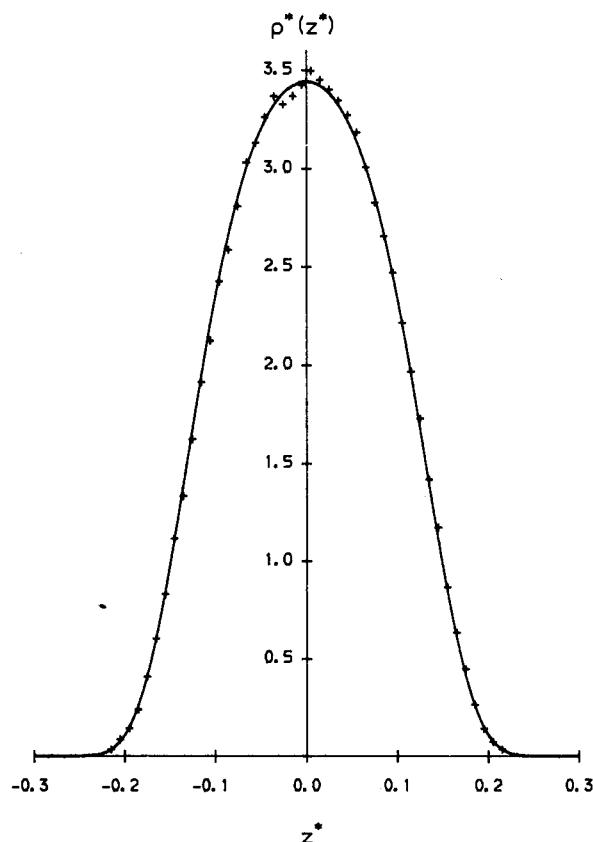


FIG. 4. $L^* = 2.2$; see caption to Fig. 2(a).

FIG. 5. $L^* = 2.1$; see caption to Fig. 2(a).FIG. 6. $L^* = 2.0$; see caption to Fig. 2(a).

interactions. At very small wall separation the attractive wall-fluid potential is just increasing the effective chemical potential of the fluid. For our choice of parameters, the changes in structure displayed in Figs. 2–6 occurred with little variation in the amount of fluid in the pore (see the tabulated values of $\langle N \rangle$). However, for $L^* < 1.6$, fluid would be squeezed out of the pore by the dominating effect of the intersecting repulsive wall fields. In this region, the system approaches the extreme confinement limit given by the potential distribution theorem, Eq. (4); i.e., $n^*(z^*) \rightarrow \exp\{\mu^*/T^*\}$.¹⁰

In summary, we conclude that whenever simulation experiments on atomic fluids confined between planar slits enter the regime $\tilde{L} < \tilde{\sigma}$, the one-body profile structure will be of the form (14). Thus, the global density structure of fluids confined to planar symmetric pores in the quasi-two-dimensional regime is described by just two parameters [α and $n^*(0)$], governed by a generalized set of thermodynamic field variables $\{T, \mu, L$ and the wall-field parameters}.¹¹

IV. GENERALIZATIONS

A straightforward generalization of the quasi-two-dimensional regime can be applied to fluid mixtures of atomic species confined between planar walls. Here, the only significant new point concerns the definition of L and \tilde{L} ; i.e., the position of the walls. For example, consider a binary mixture of atoms (A,B) absorbed in a solid pore composed of atoms of type C (where we will ignore corrugations of the solid surface).¹² There are now five core-core repulsions of relevance; namely, diameters σ_{AA} , σ_{BB} , σ_{AB} , σ_{AC} , and σ_{BC} . When $\sigma_{AC} \neq \sigma_{BC}$ it follows that the binary fluid mixture is actually confined by two pairs of planar walls; i.e., the centers of the smaller sized atoms (say, type A) occupy a larger volume ($\sigma_{AC} \langle \sigma_{BC} \Rightarrow L_A \rangle L_B$). This also means that the quasi-two-dimensional regime of species A is smaller than that of species B; i.e., using the language of Sec. II, $\tilde{L}_A < \tilde{\sigma}_{AA}$ is needed before the smaller atoms enter the quasi-two-dimensional regime but $(\tilde{L}_A + \tilde{L}_B) < 2\tilde{\sigma}_{AB}$ is sufficient to force the B atoms into lower dimensionality. Consider now the generalization of sum rule (9) to a binary mixture:

$$\begin{aligned}
 & -kT \frac{\partial \ln\{n_A(z_1)\}}{\partial z_1} \\
 & = \int_{-\infty}^{\infty} dz_2 \{ \rho_A(z_2) [h_0(z_1, z_2)_{AA} - h_0(-z_1, z_2)_{AA}] \\
 & \quad \times \phi'_A(z_2 + L_A/2) + \rho_B(z_2) [h_0(z_1, z_2)_{AB} \\
 & \quad - h_0(-z_1, z_2)_{AB}] \phi'_B(z_2 + L_B/2) \} \quad (17)
 \end{aligned}$$

and similarly for $A \leftrightarrow B$. The same arguments that led to Eq. (12) apply equally to the first term in the integrand of Eq. (17) [provided $\tilde{L}_A < \tilde{\sigma}_{AA}$] and then also to the second term [provided $(\tilde{L}_A + \tilde{L}_B) < 2\tilde{\sigma}_{AB}$]. For a general fluid mixture of atoms confined to a symmetric planar pore, the density profile of A atoms is of the form Eq. (14) whenever $\tilde{L}_A < \tilde{\sigma}_{AA}$ and $(\tilde{L}_A + \tilde{L}_i) < 2\tilde{\sigma}_{Ai}$, where i runs over all of the other fluid species. Thus, the universal profile form (14a) holds for a particular species of the mixture whenever that species is confined to its quasi-two-dimensional regime.

Let us now briefly consider the situation with regard to confined molecular fluids. Similar to the mixture case discussed above, we must first generalize the concept of a containing wall. For example, consider hard ellipsoids impinging on a strongly repulsive solid wall. When corrugation of the solid surface is ignored (i.e., assuming planar symmetry) it follows that when an ellipsoid lies parallel to the wall its center can penetrate further than when it lies end on. The standard way to describe this is to write the wall field in the form $\phi(z, \omega)$ where z is the center of mass coordinate and ω denotes the angles defining the orientation of a molecule with respect to the walls. Thus, in the language of Sec. II, we now have $\tilde{L}(\omega)$; i.e., there is now a distribution of walls which each molecule can experience depending on its orientation. The generalization of sum rule (9) is straightforward, one simply gets an equation for $\partial \ln\{n(z_1, \omega_1)\}/\partial z_1$ at fixed ω_1 . However, the integral on the right-hand side of Eq. (9) will now include an integration over all values of the orientation of molecule 2: (ω_2). Since the concept of a quasi-two-dimensional regime can be readily extended to apply at fixed values of the orientation of a tagged particle, it is possible that Eq. (14) might also be applicable to strongly confined molecular fluids, at fixed values of ω .

Generalizations of Eq. (14) to nonplanar geometries are also problematical. The most interesting case would be the quasi-one-dimensional regime of fluids confined to cylindrical pores. Namely, when $\tilde{D} < \tilde{\sigma}$, where \tilde{D} denotes the effective pore diameter (analogous to \tilde{L}) the fluid particles cannot pass one another (which is the signature of one-dimensional atomic and molecular systems). The analog of sum rule (9) in cylindrical symmetry [i.e., $v(s)$] is

$$-kT \frac{\partial \ln\{n(s_1)\}}{\partial s_1} = 2 \int_0^\infty ds_2 s_2 \rho(s_2) v'(s_2) \int_0^{\pi/2} d\theta_{12} \cos \theta_{12} \times [h_0(s_1, s_2, \theta_{12}) - h_0(s_1, s_2, \pi - \theta_{12})], \quad (18a)$$

where θ_{12} denotes the relative orientation of the radial vectors \mathbf{s}_1 and \mathbf{s}_2 and

$$h_0(s_1, s_2, \theta_{12}) \equiv \int_{-\infty}^\infty dx_{12} [g(|x_{12}|, s_1, s_2, \theta_{12}) - 1]. \quad (18b)$$

The presence of the angular integration on the right-hand side of (18a) appears to present a serious hurdle to the generation of a simple analog of (11). In particular, the criterion $\tilde{D} < \tilde{\sigma}$ requires one to think in terms of the interatomic separation; $r_{12} = (s_{12}^2 + x_{12}^2)^{1/2}$. One suspects that if it proved possible to assign a universal profile structure to the quasi-one-dimensional regime, analogous to Eq. (14), it could well turn out to be a complicated function of s .

V. CONCLUSIONS

In this paper we have examined the form of the singlet density function for fluids inside model pores when the pore width becomes small enough to reduce the effective dimensionality of the fluid. For the case of atomic fluids (including mixtures) confined within narrow planar slits, we proposed

a universal form for the density profile [Eq. (14)]. This prediction was verified by computer simulation of LJ fluid inside the quasi-two-dimensional regime. One immediate consequence of our results is that density profiles of fluids in narrow slits are known much more accurately than might otherwise be perceived. We have briefly considered the extension of our treatment to molecular fluids and cylindrical pore geometries.

ACKNOWLEDGMENTS

P. A. and J. R. H. are indebted to Dr. F. van Swol for incisive comments. P. A. thanks the SERC for a studentship and British Petroleum for a CASE award. J. P. R. B. W. thanks the British Petroleum Company plc for permission to publish this work.

¹See, for example, B. V. Derjaguin and N. V. Churaev, in *Fluid Interfacial Phenomena*, edited by C. A. Croxton (Wiley, New York, 1986); W. F. Saam and M. W. Cole, *Phys. Rev. B* **11**, 1086 (1975); B. C. Freasier and S. Nordholm, *J. Chem. Phys.* **79**, 4431 (1983); R. Evans and P. Tarazona, *Phys. Rev. Lett.* **52**, 557 (1984); R. Evans and U. Marini Bettolo Marconi, *Chem. Phys. Lett.* **114**, 415 (1985); *Phys. Rev. A* **32**, 3817 (1985); R. Evans, U. Marini Bettolo Marconi, and P. Tarazona, *J. Chem. Soc. Faraday Trans. 2* **82**, 1763 (1986); *J. Chem. Phys.* **84**, 2376 (1986); B. K. Peterson, J. P. R. B. Walton, and K. E. Gubbins, *J. Chem. Soc. Faraday Trans. 2* **82**, 1789 (1986); Z. Tan, F. van Swol, and K. E. Gubbins, *Mol. Phys.* **62**, 1213 (1987); P. Tarazona and L. Vicente, *ibid.* **56**, 557 (1985); E. Bruno, U. Marini Bettolo Marconi, and R. Evans, *Physica A* **141**, 187 (1987); P. C. Ball and R. Evans, *Eur. Lett.* **4**, 715 (1987); G. Mason, *Proc. R. Soc. London Ser. A* **415**, 453 (1988).

²R. Evans and U. Marini Bettolo Marconi, *J. Chem. Phys.* **86**, 7138 (1987).

³J. J. Magda, M. Tirrell, and H. T. Davis, *J. Chem. Phys.* **83**, 1888 (1985); J. P. R. B. Walton and N. Quirke, *Chem. Phys. Lett.* **129**, 382 (1986); G. S. Heffelfinger, F. van Swol, and K. E. Gubbins, *Mol. Phys.* **61**, 1381 (1987); B. K. Peterson and K. E. Gubbins, *ibid.* **62**, 215 (1987); A. Z. Panagiotopoulos, *ibid.* **62**, 701 (1987); T. K. Vanderlick and H. T. Davis, *J. Chem. Phys.* **87**, 1791 (1987); B. K. Peterson, K. E. Gubbins, G. S. Heffelfinger, U. Marini Bettolo Marconi, and F. van Swol, *ibid.* **88**, 6487 (1988); P. C. Ball and R. Evans, *Mol. Phys.* **63**, 159 (1988); J. G. Powles, G. Rickayzen, and M. L. Williams, *ibid.* **64**, 33 (1988); G. S. Heffelfinger, F. van Swol, and K. E. Gubbins, *J. Chem. Phys.* **89**, 5202 (1988); D. Nicolaidis and R. Evans, *Phys. Rev. B* **39**, 9336 (1989).

⁴A. Robledo and J. S. Rowlinson, *Mol. Phys.* **58**, 711 (1986).

⁵B. Widom, *J. Chem. Phys.* **39**, 2808 (1963); J. R. Henderson, *Mol. Phys.* **50**, 741 (1983).

⁶J. R. Henderson, *Mol. Phys.* **59**, 89 (1986).

⁷R. Lovett, C. Y. Mou, and F. P. Buff, *J. Chem. Phys.* **65**, 570 (1976); M. S. Wertheim, *ibid.* **65**, 2377 (1976).

⁸V. Ya. Antonchenko, V. V. Ilyin, N. N. Makovsky, A. N. Pavlov, and V. P. Sokhan, *Mol. Phys.* **52**, 345 (1984).

⁹J. P. R. B. Walton and N. Quirke, *Mol. Sim.* **2**, 361 (1989); and references therein.

¹⁰Since our fluid temperature is greater than the two-dimensional liquid-vapor critical point temperature, it follows that we do not anticipate the presence of a pore-emptying phase transition (capillary evaporation) at some value of L in the approach to the extreme confinement limit; as discussed by P. Tarazona, U. Marini Bettolo Marconi, and R. Evans, *Mol. Phys.* **60**, 573 (1987). However, a freezing transition to a quasi-two-dimensional solid might occur at smaller values of L . In fact, our $L^* = 2.0$ system has an effective two-dimensional density ($\rho_{2d} \equiv \langle N \rangle / A$) that lies close to the freezing line of the two-dimensional Lennard-Jones system; see J. A. Barker, D. Henderson, and F. F. Abraham, *Physica A* **106**, 226 (1981). Projection of the final particle coordinates onto the XY plane confirmed that each of our systems was indeed a fluid state, with the smallest system possessing the greatest amount of local hexagonal order; we are indebted to Dr. F. van Swol for drawing this procedure to our attention.

¹¹For nonsymmetric planar geometry (different walls), one would require

two more parameters to maintain the level of accuracy involved in Eq. (14a); i.e. here, the quasi-two-dimensional regime would be of the form $n(z) = n(0)\exp\{az + bz^2 + cz^3\}$.

¹²Modeling inert solid surfaces as planar walls appears to be a reasonable treatment of solid-fluid interfaces, but one must note that in real porous systems the presence of surface corrugations is likely to significantly re-

duce the region of fluid behavior; i.e., wall corrugations induce capillary solidification, as discussed by M. Schoen, D. J. Diestler, and J. H. Cushman, *J. Chem. Phys.* **87**, 5464 (1987).

¹³In particular, $\rho_s = 0.019 \text{ \AA}^{-3}$ has been used extensively to model Ar on CO_2 ; as used in pore-fluid simulations by J. E. Lane and T. H. Spurling, *Aust. J. Chem.* **33**, 231 (1980).