

**Fluids Inside a Pore — An Integral-Equation Approach**

**I. General Formalism and Hard Spheres inside Spherical and Slit Pores**

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## ABSTRACT

Integral equations for density profiles of fluids inside a slit pore and a spherical pore are derived using an **Ornstein-Zernike** system of equations. For a hard-sphere fluid we specialize to a Percus-Yevick (PY) closure and a hypernetted-chain (HNC) closure, and also consider the **BBGKY** hierarchy with a kind of superposition-approximation(SA) closure. The bulk correlation needed in the **OZ system** of equations is obtained from the PY approximation. These approximations, which will be referred as the **PY/PY** and the **HNC/PY** approximations and the **BBGKY-SA** scheme, are applied to a pure hard-sphere fluid. It is shown that the **BBGKY-SA** equation is the same as the HNC equation used with a simple approximation for bulk direct correlation functions. The density profiles, partition coefficients, and solvation forces for the hard-sphere fluids inside a slit and a spherical pore are calculated and compared with simulation results. It turns out that the **PY/PY** approximation give us a better overall agreement with simulations than either the **HNC/PY** approximation or the **BBGKY-SA** scheme in the slit-pore system. However, the **PY/PY** approximation yields some unphysical results for high concentrations and certain values of the ratio of **spherical-pore diameter** to hard-sphere diameter, while the **HNC/PY** approximation is the best among the three approximations in the spherical-pore system when compared with simulation results. A non-local **density-functional** form of closure, introduced by **Blum** and **Stell** for the flat-wall problem, is **also** discussed, but not assessed numerically.

## I. INTRODUCTION

Recently, the structure and thermodynamics of fluids inside micropores have attracted wide **attention**<sup>1–11</sup>. This is because such systems are not only related to various **separation processes** such as adsorption, exclusion chromatography and membrane transport, but they also exhibit a richer variety of thermodynamic<sup>1</sup> and structural behavior than bulk fluid systems. **Glandt** and also Post and **Glandt**<sup>2</sup> have considered the partitioning between the pore and bulk phases and obtained the density expansion of the density profile inside various pores. **McQuarrie** et al<sup>3</sup> have considered the **virial** expansion of the grand potential for the particles inside spherical and slit pores. Computer simulations of a spherical<sup>4</sup>, **slit-like**<sup>5,6</sup> and cylindrical **pore**<sup>7,8</sup> have been carried out for **hard-sphere**<sup>4,5,7</sup> and Lennard-Jones **fluids**<sup>6,8</sup>. Integral-equation theories for fluids inside a slit pore have been investigated by means of a BBGKY hierarchy with a kind of superposition approximation<sup>5</sup> (using a method in which both bulk and average densities have to be inputted), as well as a shielding approximation<sup>9</sup>, in which the resulting density profile is a product of the density profile of a single-wall and an exponential factor. In this approximation for a hard-sphere fluid, the contact value of particles at the surface of a slit pore is the same as the contact value of hard spheres in contact with a single wall, which is not necessarily a good approximation for a small pore. Some other methods, such as the **generalized Van der Waals theory**<sup>10</sup> and the use of a simple one-dimensional **model**<sup>11</sup> have also been applied to the slit-pore problem. To our knowledge, there have heretofore been no general integral-equation theories for fluids inside a spherical pore, which we shall develop in this paper.

Unlike the system of a semi-infinite fluid against a single wall, a fluid inside a single spherical micropore is a finite closed system. As a result, the homogeneous bulk phase that is the most appropriate reference system to use in describing the confined fluid is not so obvious. One choice is to take the homogeneous system which has the same chemical potential as the fluid inside a pore. However, the chemical potential is often not so easy to calculate, either by computer simulations or by

means of integral equations. Therefore, this choice, as it has just been described, is often not useful in establishing the relationship between bulk and fluid in a pore. However, **this** choice can be described in an alternative way. That is, the bulk phase corresponding to the confined phase is taken to be the homogeneous system that is found when the external force for maintaining the inhomogeneity of a system in a grand **ensemble**<sup>12</sup> is turned off. We find that the use of this reference state (which is not new) is extremely convenient in deriving and understanding the integral equations for pair correlations in confined fluids.

As the first of a series of papers on fluids confined to micropores, the purpose of this paper is to establish integral equations for a fluid inside of a spherical and slit-like pores by using two methods: the Ornstein-Zernike (**OZ**) equation<sup>12</sup> and the BBGKY hierarchy<sup>13</sup>. The OZ equation is given a formally exact closure from which the Percus-Yevick (PY) closure and hypernetted-chain (HNC) closure are obtained with the bulk correlation needed in the OZ system of equations obtained from the PY approximation. The **BBGKY**<sup>13</sup> hierarchy is closed with a kind of superposition approximation (**SA**)<sup>5,14</sup> closure. These approximations will be referred to here as the **PY/PY** approximation, the **HNC/PY** approximation, and the BBGKY-SA scheme. Integral equations for the system of fluids inside a cylindrical pore will be the subject of another paper. It should be noted the **OZ** equation with an **HNC/MSA** closure (where MSA stands for mean spherical approximation) has already been applied to an ionic system confined between two **walls**<sup>15</sup>. Here we shall derive these equations in a nonionic case (where MSA = PY) in a different way. We obtain equivalent equations of a simpler functional form by introducing somewhat different functions from those used in ref 15.

**This** paper is organized as follows: general formulations for the fluid inside a pore in terms of the OZ equation and the BBGKY hierarchy are given in section **II** and **III** respectively. Numerical methods for solving these integral equations for a hard-sphere fluid are described in section **IV**. Quantitative results are discussed and compared with simulation **results**<sup>4,5</sup> in section V. For simplicity, we focus in **this** paper on a one-species hard-sphere system of particles inside hard spherical and

slit pores. A density-functional closure considered earlier in the bulk-fluid problem by one of us and introduced into the flat-wall problem by Blum and **Stell** may prove advantageous in considering system with attractive potentials. This is discussed in section VI.

## II. THE OZ EQUATION

A pure fluid of particles inside a spherical or slit pore can be considered as a special case of a binary mixture of two species : molecules, which are taken as hard-core molecules of diameter  $d_m$  and indicated with a subscript m, and a pore, indicated with a subscript p, which is modeled as a hard core which has a radius of  $R_p$  enclosed by a concentric hard spherical shell which **has** an inner surface of radius of  $R_p + L$  and an outer surface of radius of  $R'_p$ . It is obvious that we have a spherical pore *if* we take away of the inner hard core and a slit-like pore when  $R_p = \infty$ .

In terms of this model, we shall consider a simple hard-core pair potential with a soft tail between molecules

$$\begin{aligned} \beta u_{mm}(r) &= \infty \quad \text{if } r \leq d_m \\ &= \beta u_{mm}^t(r) \quad \text{otherwise} \end{aligned} \quad (2.1)$$

where  $d_m$  is the diameter of molecule species, and we let the potential between a molecule and a concentric spherical pore be

$$\begin{aligned} \beta u_{mp}(r) &= \infty \quad \text{if } r < (R_p + R_m) \\ &= \beta u_{mp}^t(r) \quad \text{if } (R_p + R_m) < r < (R_p + L - R_m) \\ &= \infty \quad \text{if } (R_p + L - R_m) < r < (R'_p + R_m) \\ &= 0 \quad \text{otherwise} \end{aligned} \quad (2.2a)$$

where  $R_m = d_m/2$  and the tail potential  $u_{mp}^t(r)$  comes from the **interaction** of a molecule with the inner hard core and the inner surface of the pore. Finally, we let

the potential between a molecule and a spherical pore be

$$\begin{aligned}\beta u_{mp}(r) &= \beta u_{mp}^t(r) \quad \text{if } 0 < r < (L - R_m) \\ &= \infty \quad \text{if } (L - R_m) < r < (R_p' + R_m) \\ &= 0 \quad \text{otherwise}\end{aligned}\tag{2.2b}$$

The OZ equation is directly applicable to this binary mixture. We have,

$$h_{mm} - c_{mm} = \rho_m h_{mm} * c_{mm} + \rho_p h_{mp} * c_{pm}\tag{2.3}$$

$$\begin{aligned}h_{mp} - c_{mp} &= \rho_m h_{mm} * c_{mp} + \rho_p h_{mp} * c_{pp} \\ &= \rho_m h_{pm} * c_{mm} + \rho_p h_{pp} * c_{pm}\end{aligned}\tag{2.4}$$

where  $c_{ij}$ ,  $h_{ij}$  are the **direct** and indirect pair correlation functions between particle species  $i$  and  $j$  respectively, and  $\rho_i$  is the number density of particle of species  $i$ .

Since we only consider one pore, that is,  $\rho_p \rightarrow 0$ , equation (2.3) becomes the OZ equation for a one-component hard-core fluid. We have

$$h_{mm} - c_{mm} = \rho_m h_{mm} * c_{mm}\tag{2.5}$$

In the simplest case of hard spheres, a solution is well known if the **Percus-Yevick** (PY) closure is **used**<sup>16</sup>. Equation (2.4) in this **limit** is also simplified:

$$\begin{aligned}h_{mp} - c_{mp} &= \rho_m h_{mm} * c_{mp} \\ &= \rho_m h_{pm} * c_{mm}\end{aligned}\tag{2.6}$$

which can be rewritten as

$$\begin{aligned}g_{mp}(r) &= C_{mp}(r) + \rho_m h_{mm} * C_{mp} \\ &= C_{mp}(r) + \rho_m c_{mm} * g_{mp}\end{aligned}\tag{2.7}$$

where we have **used** equation (2.5) and the relation

$$g_{mp}(r) \equiv h_{mp}(r) + 1\tag{2.8}$$

Here  $g_{mp}(r)$  is the density distribution function of molecules when the pore is fixed at the origin. We have also introduced

$$C_{mp}(r) \equiv c_{mp}(r) + a_1\tag{2.9a}$$

where  $a_1$  is

$$a_1 \equiv 1 - \rho_m \tilde{c}_{mm}(0) \quad (2.9b)$$

with the tilde denoting a 3-D Fourier transformation.

Regarding  $h_{mm}$  and  $c_{mm}$  as known functions, one can introduce an exact closure by giving a second exact relation between  $h_{mp}$  and  $c_{mp}$ , independent of (2.6), which in general must be expected to also involve bulk correlation functions. For example we can write<sup>13</sup>

$$c_{mp}(r) = f_{mp}(r)[g_{mp}(r) - c_{mp}(r)] + e_{mp}(r)d_{mp}(r) \quad (2.10a)$$

where  $f_{mp}(r)$  is the Mayer f-function,  $e_{mp} = f_{mp} + 1$ , and  $d_{mp}(r)$  is a tail function. Alternatively, we can write

$$c_{mp}(r) = h_{mp}(r) - \ln g_{mp}(r) - \beta u_{mp} - B_{mp}(r) \quad (2.10b)$$

where  $B_{mp}(r)$  is a bridge-function<sup>13</sup>. Neglect of  $d_{mp}$  and  $B_{mp}$  yield PY and HNC approximations, respectively, which we consider below. Closures of a somewhat different “non-local” form that may prove especially useful when considering  $u_{mm}$  and  $u_{mp}$  that have soft attractive contributions are discussed in section VI.

If one use the analytical solution for  $c_{mm}(r)$  in the PY approximation<sup>12,16</sup> for hard spheres, then, one finds

$$a_1 = \frac{(1 + 2\eta)^2}{(1 - \eta)^4} \quad (2.11)$$

where  $\eta$  is the packing fraction, which is defined as

$$\eta \equiv \frac{\pi}{6} \rho_m d_m^3 \quad (2.12)$$

If we turn off the external force ( $\beta u_{mp} = 0$ ), then equation (2.7) with the PY closure or the HNC closure<sup>12</sup> will give us a solution

$$g_{mp}(r) \equiv \frac{\rho_m(r)}{\rho_m} = 1$$

where  $\rho_m(r)$  is the density profile of the molecules inside a pore. Therefore, the solution of the OZ equations will give us the mean distribution of particles in the

inner sphere which is in equilibrium with a homogeneous system with a bulk density of  $\rho_m$ . Now we divide our treatment of the equations for spherical and slit pores into two subsections. At this point, for computational simplicity, we consider the most easily handled case of the hard-sphere fluid in hard-wall pores, with the  $u_{mm}^t(\mathbf{r})$  of equation (2.1) and  $u_{mp}^t(\mathbf{r})$  of (2.2) set equal to zero.

### 1. A Slit-like Pore

If we use the PY closure<sup>12</sup>, then we have

$$h_{mp}(\mathbf{r}) = -1 \quad \text{if } r < (R_p + R_m) \text{ or } (R_p + L - R_m) < r < (R'_p + R_m) \quad (2.13a)$$

$$c_{mp}(\mathbf{r}) = 0 \quad \text{if } (R_p + R_m) < r < (R_p + L - R_m) \text{ or } r > (R'_p + R_m) \quad (2.13b)$$

where we have used equation (2.2a). Or, equivalently, from equations (2.8) and (2.9),

$$g_{mp}(\mathbf{r}) = 0 \quad \text{if } r < (R_p + R_m) \text{ or } (R_p + L - R_m) < r < (R'_p + R_m) \quad (2.14a)$$

$$C_{mp}(\mathbf{r}) = a_1 \quad \text{if } (R_p + R_m) < r < (R_p + L - R_m) \text{ or } r > (R'_p + R_m) \quad (2.14b)$$

By using bipolar coordinates and equation (2.14a), the second equality of equation (2.7) becomes

$$g_{mp}(\mathbf{r}) = C_{mp}(\mathbf{r}) + \frac{2\pi\rho_m}{r} \int_{(R_p+R_m)}^{(R_p+L-R_m)} sg_{mp}(s) ds \int_{|r-s|}^{(r+s)} tc_{mm}(t) dt \\ + \frac{2\pi\rho_m}{r} \int_{(R'_p+R_m)}^{\infty} sg_{mp}(s) ds \int_{|r-s|}^{(r+s)} tc_{mm}(t) dt \quad (2.15)$$

By noting the fact that<sup>16</sup>

$$c_{mm}^{PY}(\mathbf{r}) = 0 \quad \text{if } r > d_m \quad (2.16)$$

it is easy to see that the last term in equation (2.15) is zero if  $r < (R_p + L - R_m)$

$$g_{mp}(\mathbf{r}) = C_{mp}(\mathbf{r}) + \frac{2\pi\rho_m}{r} \int_{(R_p+R_m)}^{(R_p+L-R_m)} sg_{mp}(s) ds \int_{|r-s|}^{(r+s)} tc_{mm}(t) dt. \quad (2.17)$$

That means the distribution of particles inside the hard spherical shell is independent of how thick the hard shell is, as it should be. Similarly, it is easy to show



that the distribution of particles outside a hard spherical shell only depends on the radius of the outer sphere,  $R'_p$ . Therefore, we see that the solution of the OZ equations will satisfy these exact conditions if one uses the PY approximation in the bulk-fluid regions.

Since the form of the pair correlation functions  $g_{mp}(r)$  inside a spherical shell is independent of the radius of the outer sphere,  $R'_p$ , from now on, we shall let

$$R'_p \rightarrow \infty \quad (2.18)$$

for simplicity. In this limit, it is obvious that equation (2.17) is valid for all distances  $r$  if one reapplies equation (2.14a) to equation (2.7). Then it is easy to prove from equation (2.17)

$$C_{mp}(r) \equiv 0 \quad \text{if } r > (R_p + L + R_m) \text{ and } r < (R_p - R_m) \quad (2.19)$$

where we have used equation (2.16).

In the limit of  $R_p \rightarrow \infty$ , equations (2.7) and (2.19) with the PY closure (2.13) become<sup>17</sup>, after changing coordinates to  $z = r - R_p - L/2$

$$\begin{aligned} \bar{g}_{mp}(z) &= \bar{C}_{mp}(z) + \rho_m \int d\mathbf{r}' h_{mm}(|\mathbf{r} - \mathbf{r}'|) \bar{C}_{mp}(z') \\ &= \bar{C}_{mp}(z) + \rho_m \int d\mathbf{r}' c_{mm}(|\mathbf{r} - \mathbf{r}'|) \bar{g}_{mp}(z') \end{aligned} \quad (2.20)$$

$$\bar{g}_{mp}(z) = 0 \quad z < -L/2 + R_m \text{ or } z > L/2 - R_m \quad (2.21a)$$

$$\bar{C}_{mp}(z) = 0 \quad z < -L/2 - R_m \text{ or } z > L/2 + R_m \quad (2.21b)$$

$$\bar{C}_{mp}(z) = a_1, \quad -L/2 + R_m < z < L/2 - R_m \quad (2.21c)$$

where  $\bar{y}(z) \equiv y(r - R_p - L/2)$  and  $y$  is the  $g_{mp}$  or  $C_{mp}$  function. It is easy to verify that equation (2.20) with closure (2.21) is invariant under the transformation  $a \leftrightarrow -z$ . Therefore the solution of these equations will be symmetric, as it should be.

The partition coefficient<sup>2</sup> is defined as the ratio of the averaged density  $\bar{\rho}_m$  inside the core to the bulk density,  $\rho$

$$K \equiv \frac{\bar{\rho}_m}{\rho_m}. \quad (2.22)$$

where  $\bar{\rho}_m$  is the average density inside a pore. For a slit pore, we have

$$K \equiv \frac{2 \int_0^{L/2-R_m} \bar{g}_{mp}(z) dz}{L} \quad (2.22a)$$

Using the **1-D** Fourier transformation of the **second** equality of equation (2.20) with equations (2.21b,c), we have,

$$K = K_0 + \frac{2}{La_1} \left\{ \int_{(L/2-R_m)}^{(L/2+R_m)} \bar{C}_{mp(E)} dz \right\} \quad (2.22b)$$

where

$$K_0 \equiv (1 - A)$$

is the so-called Henry's-law **constant**<sup>2(c)</sup> for a slit pore, and  $\lambda \equiv d_m/L$ .

As  $\rho_m \rightarrow 0$ , we have, from the first equality of equations (2.20) and equation (2.21a), if  $(-L/2 - R_m) < z < (-L/2 + R_m)$  or  $(L/2 - R_m) < z < (L/2 + R_m)$ ,

$$\bar{C}_{mp}(z) = \bar{g}_{mp}(z) = 0 \quad (2.23)$$

Therefore, the second part of equation (2.22b) goes to zero in this limit and the partition coefficient calculated via equation (2.22b) has the right low-concentration **limit**<sup>18</sup>.

$$K \rightarrow K_0 \quad \text{if } \rho_m \rightarrow 0 \quad (2.24a)$$

In addition, it is easy to show that equation (2.22b) satisfies the exact limiting conditions

$$K \rightarrow 1 \quad \text{if } \lambda \rightarrow 0 \quad (2.24b)$$

$$K \rightarrow 0 \quad \text{if } \lambda \rightarrow 1 \quad (2.24c)$$

The Gibbs absorption for a slit pore, which satisfies the equation<sup>1</sup>

$$\Gamma = \int_{-L/2+R_m}^{L/2-R_m} dz (\rho_m(z) - \rho_m), \quad (2.25)$$

has a direct relationship with the partition coefficient

$$\Gamma = \rho_m L (K - K_0) \quad (2.26)$$

where we have used equation (2.22a), the definition of  $K_0 = 1 - \lambda$ , and  $\rho_m(z) = \rho_m \bar{g}_{mp}(z)$ . Since "the adsorption process is one of volume-filling rather than of surface-covering in **micropores**"<sup>2(c)</sup>, we shall focus on the partition coefficient instead of the Gibbs absorption,  $\Gamma$ . The solvation force<sup>1</sup> per unit area inside a **slit** pore satisfies the following equation

$$\beta f = - \int \rho_m \bar{g}_{mp}(z) \frac{d\beta \bar{u}_{mp}(z)}{dz} dz \quad (2.27)$$

which becomes

$$\beta f \equiv 2\rho_m \bar{g}_{mp}(L/2 - R_m) = 2\beta P^W \quad (2.28)$$

where we have used the **symmetry** of  $\bar{g}_{pm}(z)$  and where  $P^W$  is the pressure exerted by molecules on walls. We note that the relationship between  $\bar{u}_{mp}(z)$  and  $u_{mp}(r)$  is same as the relationship between  $\bar{g}_{mp}(z)$  and  $g_{mp}(r)$ .  $P^W$  should approach the bulk pressure as the distance  $L$  between two hard walls increases according to the exact contact-value theorem for a single hard-wall **problem**<sup>14</sup>.

## 2. A Spherical Pore

The derivation of the equations for a fluid inside a spherical pore is very similar to the **slit-pore** derivation. Therefore, we shall not dwell upon its details. By using equation (2.2b), we have the PY closure for a spherical pore

$$g_{mp}(r) = 0 \quad \text{if } r > L - R_m \quad (2.29a)$$

$$C_{mp}(r) = a_1 \quad \text{if } r < L - R_m \quad (2.29b)$$

and we also have

$$C_{mp}(r) = 0 \quad \text{if } r > L + R_m \quad (2.29c)$$

where we have used equation (2.18).

For a spherical pore, we have the partition coefficient, from its definition (equation (2.22)), given by

$$K \equiv \frac{\bar{g}_{mp}(0)}{(4/3)\pi L^3} \quad (2.30)$$

where the tilde indicates a 3-D **FFT**. Using the second equality of equation (2.7) along with equations (2.29b,c), we have

$$K = K_0 + \frac{3}{a_1 L^3} \int_{(L-R_m)}^{(L+R_m)} r^2 C_{mp}(r) dr \quad (2.31)$$

Here

$$K_0 \equiv (1 - \lambda)^3$$

is Henry's-law **constant**<sup>2(c)</sup> for a spherical pore and  $\lambda \equiv R_m/L$ .

Again, we have

$$K \rightarrow K_0 \quad \text{if } \rho_m \rightarrow 0 \quad (2.32a)$$

$$K \rightarrow 1 \quad \text{if } \lambda \rightarrow 0 \quad (2.32a)$$

$$K \rightarrow 0 \quad \text{if } \lambda \rightarrow 1 \quad (2.32b)$$

The solvation force inside a spherical pore satisfies the equation

$$\beta F = -4\pi \int r^2 \rho_m g_{mp}(r) \frac{d\beta u_{mp}(r)}{dr} dr \quad (2.33)$$

which becomes

$$\beta f \equiv \frac{\beta F}{4\pi L^2} = (1 - \lambda)^2 \rho_m g_{mp}(L - R_m) \quad (2.34)$$

if we substitute equation (2.2b) into (2.34). Therefore,

$$\frac{f}{p^B} = (1 - \lambda)^2 \quad \text{as } \rho_m \rightarrow 0 \quad (2.35)$$

where  $p^B$  is the bulk pressure which satisfied the ideal-gas behaviour as the density of molecules goes to zero.

It is worth noting that  $L$  represents here the radius of a spherical pore, whereas we have used it to denote a **distance** of separation of two **walls** in the slit pore problem.

In summary, we need to solve the equations (2.20) and (2.21) in the slit-pore problem and equations (2.7) and (2.29) in the spherical-pore problem for density profiles in the **PY/PY approximation**. In the **HNC/PY** approximation, equation (2.7) with equation

$$g_{mp}(r) = 0 \quad \text{if } r > L - R_m \quad (2.36a)$$

$$\ln g_{mp}(r) = g_{mp}(r) - C_{mp}(r) - 1 + a_1 \quad \text{if } r < L - R_m \quad (2.36b)$$

forms a closed set of equations for the spherical-pore problem, while equation (2.20) with equation

$$\bar{g}_{mp}(z) = 0 \quad z < -L/2 + R_m \text{ or } z > L/2 - R_m \quad (2.37a)$$

$$\ln \bar{g}_{mp}(z) = \bar{g}_{mp}(z) - \bar{C}_{mp}(z) - 1 + a_1 \quad \text{if } -L/2 + R_m < z < L/2 - R_m \quad (2.37b)$$

forms a closed set of equations for the slit-pore problem.

Once the density profile is obtained in either approximation, the partition coefficient is calculated from equations (2.22a) and (2.30) and the solvation force from equation (2.28) and equation (2.34) in the slit-pore and spherical-pore problems respectively.

### III. THE BBGKY HIERARCHY

The first member of the **BBGKY** hierarchy<sup>13</sup> is the equation

$$\nabla_1 g_1(\mathbf{r}_1) = -(\beta \nabla_1 \phi) g_1(\mathbf{r}_1) - \rho \beta \int \nabla_1 u(\mathbf{r}_{12}) g_2(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_2 \quad (3.1)$$

where  $g_1(\mathbf{r}_1)$  and  $g_2(\mathbf{r}_1, \mathbf{r}_2)$  are the one-particle and two-particle distribution functions respectively and  $u(\mathbf{r}_{12})$  is the pair potential between particles. The 4 is the external potential energy. We introduce a kind of superposition **approximation**<sup>5,14</sup>, given by

$$g_2(\mathbf{r}_1, \mathbf{r}_2) = g_{mm}(\mathbf{r}_{12}) g_1(\mathbf{r}_1) g_1(\mathbf{r}_2) \quad (3.2a)$$

where  $g_{mm}(\mathbf{r}_{12})$  is the distribution function of homogeneous system when the external force is turned off. Physically this ansatz reflects the assumption that spatial inhomogeneities appearing in the two-particle correlation can be expressed as the independent effect of the inhomogeneities acting on each particle. When generalized to include momentum correlation through the coordinates  $\mathbf{x}_i = (\mathbf{r}_i, \mathbf{p}_i)$ , where  $\mathbf{p}_i$  is the momentum of the  $i$ -th particle, the **ansatz**

$$g_2(\mathbf{x}_1, \mathbf{x}_2) = g_2(\mathbf{r}_{12}) g_1(\mathbf{x}_1) g_1(\mathbf{x}_2) \quad (3.2b)$$

is the one implicitly used for the contact value  $\mathbf{r}_{12} = d$  for precollisional  $\mathbf{p}_i$  by **Enskog**<sup>19a</sup> in his hard-sphere kinetic theory. More recently (3.2b) was used as the bases of the theory of the electron gas of **Singwi, Tosi, Land, and Sjölander**(STLS)<sup>19b</sup>.

Equation (3.2a) becomes the familiar **Kirkwood superposition** approximation in a special case<sup>1\*</sup>. If the only source of the spatial inhomogeneity is the field of a single molecule at  $\mathbf{r}_3$ , then,  $g_2(\mathbf{r}_1, \mathbf{r}_2)$  becomes  $g_3(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)$ , the three-particle distribution function, while  $g_1(\mathbf{r}_i) = g_{mm}(\mathbf{r}_i; \mathbf{r}_3)$  so that (3.2a) becomes

$$g_3(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) = g_{mm}(\mathbf{r}_{12})g_{mm}(\mathbf{r}_{13})g_{mm}(\mathbf{r}_{23})$$

which is just the **Kirkwood** superposition approximation for a molecular system.

If we define<sup>5</sup>  $\nabla_1 G(\mathbf{r}_{12})$  by the equation

$$\nabla_1 G(\mathbf{r}_{12}) = g_{mm}(\mathbf{r}_{12})\nabla_1 u(\mathbf{r}_{12}) \quad (3.3)$$

then, we have, after integrating over the equation (3.1) with help of equations (3.2a) and (3.3),

$$\ln g_1(\mathbf{r}_1) = -\beta\phi + C - \rho\beta \int G(\mathbf{r}_{12})g_1(\mathbf{r}_2)d\mathbf{r}_2 \quad (3.4)$$

where C is an integration constant which can be determined by turning off the external force( $\beta\phi$ ).

$$C = 4\pi\rho\beta \int_0^\infty t^2 G(t)dt \quad (3.5)$$

The main difference between equation (3.4) and a similar equation obtained in ref 5 is that our integration constant is directly connected to bulk properties and the constant of that reference is related to the average density inside a pore. The above equations in **Sec. III** are perfectly general for hard-core particles. We now specialize to the hard-sphere case, where we have<sup>6</sup>

$$\beta G(r) = \begin{cases} 0 & r > d_m \\ g_{mm}(d_m) & r < d_m \end{cases} \quad (3.6)$$

Therefore,

$$C = 8\eta g_{mm}(d_m) = \frac{4\eta(2-\eta)}{(1-\eta)^3} \quad (3.7)$$

where we have used the **Carnahan-Starling** (CS) equations of **state**<sup>12</sup> to obtain  $g_{mm}(d_m)$ .

Now, for a slit pore, using the previous notation, we have,

$$\ln \bar{g}_{mp}(z) = -\beta \bar{u}_{mp}(z) + C - \rho_m \beta \int G(|\mathbf{r} - \mathbf{r}'|) \bar{g}_{mp}(z') d\mathbf{r}' \quad (3.8)$$

When  $L \leq 2d_m$  or  $\lambda = d_m/L \geq 0.5$ , it turns out that the equation (3.8) can be manipulated analytically<sup>6</sup> to give

$$\ln \bar{g}_{mp}(z) = C + \pi \rho_m g_{mm}(d_m) [g_0(z^2 - d_m^2) + g_2] \quad (3.9)$$

where

$$g_0 \equiv \int \bar{g}_{mp}(z) dz \quad (3.10a)$$

$$g_2 \equiv \int z^2 \bar{g}_{mp}(z) dz \quad (3.10b)$$

The equation (3.9) is still a non-linear equation that must be solved for  $g_0$  and  $g_2$ . However, we can at least immediately see from it that  $\ln g_{mp}(z)$  is a function of  $z^2$  if  $\lambda = d_m/L \geq 0.5$ . The partition coefficient and solvation force for a slit pore in the BBGKY with the kind of superposition approximation given by equation (3.2a) can also be calculated from equations (2.22a) and (2.28).

For a spherical pore, we have, from equations (3.4) and (3.7),

$$\ln g_{mp}(r) = g_{mm}(d_m) \left[ 8\eta - \frac{2\pi}{r} \rho_m \int_0^{L-R_m} s g_{mp}(s) ds \int_{|r-s|}^{\min(r+s, d_m)} t dt \right] \quad (3.11)$$

It is easy to see that  $g_{mp}(r)$  is a constant inside a spherical pore when  $L \leq 2R_m$  or  $\lambda = R_m/L \geq 0.5$ . We have

$$\ln g_{mp} = \eta g_{mm}(d_m) \left( 8 - \frac{(1-\lambda)^3}{\lambda^3} g_{mp} \right) \quad (3.12)$$

At low density, we have

$$g_{mp} = \frac{\lambda^3 (8\eta g_{mm}(d_m) + 1)}{\lambda^3 + \eta g_{mm}(d_m) (1-\lambda)^3} \quad (3.13)$$

The partition coefficient and solvation force will be, if  $\lambda \geq 0.5$ ,

$$K = (1-\lambda)^3 g_{mp} \quad (3.14)$$

$$\beta f = (1 - \lambda)^2 \rho_m g_{mp} \quad (3.15)$$

where equations (2.30) and (2.34) have been used. The density expansion of equation (3.14) gives us

$$\begin{aligned} K = & (1 - \lambda)^3 \\ & + (-9\lambda^3 + 30\lambda^2 - 39\lambda + 28 - 15\lambda^{-1} + 6\lambda^{-2} - \lambda^{-3})\eta \\ & + (-63\lambda^3 + 264\lambda^2 - 507\lambda + 628 - 567\lambda^{-1} + \\ & 378\lambda^{-2} - 189\lambda^{-3} + 72\lambda^{-4} - 18\lambda^{-5} + 2\lambda^{-6})\eta^2/2 \end{aligned} \quad (3.16)$$

where the first two terms are exactly same as the result obtained in ref. 2(c).

It is interesting that the BBGKY-SA equation (3.4) can be related to the OZ equation (2.6) with the hypernetted-chain (HNC) closure<sup>12</sup>

$$\ln g_{mp}(r) = h_{mp}(r) - c_{mp}(r). \quad (3.17)$$

Combining OZ equation (2.6) with equation (3.17), we can immediately obtain equation (3.4) if we assume the bulk direct pair correlation function

$$c_{mm}(r) = -\beta G(r) \quad (3.18)$$

which is, for hard sphere molecules

$$c_{mm}(r) = \begin{cases} -g_{mm}(d_m) & r < d_m \\ 0 & r > d_m \end{cases} \quad (3.19)$$

where we have used equations (3.6). For a hard-sphere system, this is exact in the limit in which one of the molecules is a point molecule, but otherwise not as good as an approximation as the PY approximation (which is also exact in the same limit). In particular, it will violate the core condition  $g_{mm}(r) = 0$  for  $r < d_m$  when used with the  $m - m$  OZ equation. As a result, in terms of its two-particles correlation function input, we would not expect the BBGKY-SA to be as good an approximation as the HNC/PY approximation. Equation (3.18) is also used in the STLS theory<sup>10</sup>. Since there is no extended repulsive core in the electron-gas problem, the violation of the core-condition is not as serious in that approximation.



## N . NUMERICAL METHODS

For the spherical-pore problem, as the diameter of a pore  $d_p \rightarrow \infty$ , the solution of equations (2.7) with a PY closure relation (2.29) should approach the solution of the problem for hard spheres **against** one single hard wall with the PY closure for both the wall-particle and bulk **problems**. In order to solve equations (2.7) **and** (2.29), we use a reference direct pair-correlation function which is obtained from the analytical solution of the binary hard-sphere mixture in the **PY approximation**<sup>16</sup>. In our notation, **this** gives us

$$C_{mp}^{ref}(r) = c_{mp}^{ref}(r) + a_1 \quad (4.1)$$

$$c_{mp}^{ref}(r) \equiv c_{12}^{PY}(-d_p, d_m, \rho_p, \rho_m, -r) \quad (4.2)$$

where  $c_{12}^{PY}(d_1, d_2, \rho_1, \rho_2, r)$  is the analytical solution of the distinct direct pair correlation of a binary **PY** hard sphere mixture with hard-sphere diameters  $d_1, d_2$  and densities  $\rho_1, \rho_2$  respectively<sup>16</sup>. As a result, we have

$$C_{mp}^{ref}(r) = \begin{cases} a_1 & \text{if } r \leq (d_p - d_m)/2 \\ (bx^2 - 4d_{pm}dx^3 + dx^4)/r & \text{if } (d_p - d_m)/2 < r < (d_p + d_m)/2 \\ 0 & \text{if } r > (d_p + d_m)/2 \end{cases} \quad (4.3)$$

where

$$z = (d_p + d_m)/2 - r \quad (4.3a)$$

$$d_{pm} = (d_p + d_m)/2 \quad (4.3b)$$

$$b = -3\eta_m d_m g_{mm}^{PY}(d_m) g_{12} \quad (4.3c)$$

$$d = \frac{1}{2}\eta_m a_1 \quad (4.3d)$$

$$g_{12} = (-d_p g_{mm}(d_m) + d_m g_{pp}) \quad (4.3e)$$

$$g_{pp} = [(1 - \eta) - \frac{3}{2}\eta_m d_m^2 d_p] / (1 - \eta)^2 \quad (4.3f)$$

$$g_{mm}^{PY}(d_m) = \frac{(1 + 0.5\eta)}{(1 - \eta)^2} \quad (4.3g)$$

$$\eta_m = \pi/6\rho_m \quad (4.3h)$$

$$d_p = 2L \quad (4.3i)$$

which **approaches** the analytical results of a PY hard-wall **problem**<sup>17</sup> as  $d_p \rightarrow m$ .

Then, the second equality of the equation (2.8) becomes

$$g_{mp}(r) = C_{mp}(r) + \rho_m h_{mm} * C_{mp}^{ref} + \rho_m h_{mm} * \Delta C_{mp} \quad (4.4)$$

where

$$\Delta C_{mp}(r) = C_{mp}(r) - C_{mp}^{ref}(r) \quad (4.5)$$

which is nonzero only in the region  $(d_p - d_m)/2 < r < (d_p + d_m)/2$ . Equations (4.4) with (2.29) can be easily solved by an iterative method through the FFT technique.

The equation (3.11) which is derived from the BBGKY hierarchy for the spherical-pore problem can be easily solved by using **3-D FFT** methods.

The solution for a slit pore is very similar to that of a spherical pore. First, since both  $\bar{g}_{mp}(z)$  and  $\bar{C}_{mp}(z)$  are even functions, we have,

$$y(k) \equiv \int_{-\infty}^{\infty} dz e^{ikz} y(z) = 2 \int_0^{\infty} dz \cos(kz) y(z) \quad (4.6)$$

where  $y(k)$  is one-dimensional fourier transform of  $y(z)$ , which is an even function, and  $y$  is  $\bar{C}_{mp}(z)$  or  $\bar{g}_{mp}(z)$  function. Then equation (2.20) becomes

$$\bar{g}_{mp}(k) - \bar{C}_{mp}(k) = \rho_m \tilde{h}_{mm}(k) \bar{C}_{mp}(k) \quad (4.7)$$

where

$$\tilde{h}_{mm}(k) \equiv \frac{4\pi}{k} \int_0^{\infty} dr r \sin(kr) h_{mm}(r) \quad (4.8)$$

Multiplying equation (4.7) by  $e^{-ikz}/(2\pi)$  and integrating over  $k$  from  $-\infty$  to  $m$ , We have,

$$\bar{g}_{mp}(z) - \bar{C}_{mp}(z) = \frac{\rho_m}{\pi} \int_0^{\infty} dk \cos(kz) \tilde{h}_{mm}(k) \bar{C}_{mp}(k) \quad (4.9)$$

since both  $\tilde{h}_{mm}(k)$  and  $\bar{C}_{mp}(k)$  are even functions.

$\bar{C}_{mp}(z)$  can **also** be divided into a reference part and fluctuation part just as  $C_{mp}(r)$  is in equation (4.5):

$$\Delta \bar{C}_{mp}(z) = \bar{C}_{mp}(z) - \bar{C}_{mp}^{ref}(z) \quad (4.10)$$

Here, the reference part will be taken from the analytical solution of the PY hard-wall **problem**<sup>17</sup>. Substituting equation (4.10) into (4.9), we have a **equation** similar to (4.4) which can be solved by an iterative method.

The equation (3.8), which is derived from BBGKY hierarchy for the slit-pore problem, can be easily solved iteratively by using 1-D **FFT** methods.

For the **HNC/PY** approximation, the method of solving integral equations is basically the same. We shall therefore not give the detailed development here.

## V. QUANTITATIVE RESULTS

### 1. Results for a Slit Pore

Partition coefficients,  $K/K_0$ , are shown in Figs 1-2, where they are given as functions of the ratio of molecular diameter to distance between two hard walls,  $d_m/L$ , and of the bulk density of molecules, calculated in the **PY/PY** and BBGKY-SA schemes. It can be seen that the average density obtained from the BBGKY-SA is higher than that obtained from the **PY/PY** approximation.

The pressure acting on the wall,  $\beta P^W d_m^3$ , which is obtained by the simulation method<sup>5</sup>, the BBGKY-SA, and the **PY/PY** approximation, is plotted as a function of  $L/d_m - 1$  in Fig.3. It is seen that at a very small separation of walls  $[(L-d_m)/d_m < 2/3]$ , the results of **PY/PY** give us good agreement with simulations. However, because the **PY/PY** approximation does not satisfy the contact-value theorem at one single hard-wall **problem**<sup>14</sup>, the pressure obtained by this approximation does not approach to the bulk pressure as the distance between two walls ( $L$ ) increases, while the results obtained from BBGKY-SA schemes do have the right **limit** and are in rough agreement with simulation results for  $(L-d_m)/d_m > 2/3$  although the BBGKY-SA pressure appears to approach the bulk density much faster than the simulation pressure does. It should be noted that here and hereafter in this paper the bulk pressure is calculated from the Carnahan-Starling equation of **state**<sup>12</sup>.

The solvation force (which is twice as large as the molecular pressure acting on the wall) as a function of density is also shown in Fig.4.

Results of density profiles obtained from the **PY/PY** and **HNC/PY** approximations as well as the BBGKY-SA approximation are compared with the simulation results<sup>5</sup> in Fig.5. It turns out that the **PY/PY** approximation gives us better results than either the BBGKY-SA or the **HNC/PY** approximation. It should be noted that results of the BBGKY-SA equation obtained in ref. 5 give good agreement with simulations when  $L < 2d_m$ . This is because simulation values of average densities are inputted in that reference. Therefore, the resulting equation is a semi-empirical equation in such comparisons.

## 2. Results for a Spherical Pore

Partition coefficients,  $K/K_0$ , calculated by means of the **PY/PY** and **HNC/PY** approximations and the BBGKY-SA are plotted as a function of the diameter ratio,  $\lambda$ , at different densities in Fig.6. It turns out that results obtained from the **PY/PY** approximation are again smaller than that obtained by the BBGKY-SA (just as in the case of a slit pore) and the **HNC/PY** approximation.

Partition coefficients as a function of reduced molecular density are also plotted in Fig.7. In Fig.8, the reduced solvation force,  $f/[p^B(1-\lambda)^2]$ , as a function of molecule/pore-diameter ratio shows an oscillating structure as shown in Fig.3. Again, we see that only the BBGKY-SA satisfies the contact value theorem as  $\lambda \rightarrow 0$ . The reduced solvation force as a function of the reduced molecular density at the fixed diameter ratio is shown in Fig.9.

Results of density profiles for the particles inside a spherical pore are plotted as a function of distance in Fig.10. In Fig.10f, results obtained by using the **PY/PY** and **HNC/PY** approximations and the BBGKY-SA scheme have been compared with a recent simulation result<sup>6</sup>. It is seen that **HNC/PY** results are the best among three approximations compared with the simulation data. The results from the BBGKY-SA scheme show an unrealistic crystallization of fluids inside a spherical

pore (fig.10f), while the **PY/PY** approximation gives us **unphysical** (negative)  $g_{mp}(r)$  results (Fig.10b,d) at certain values of  $\lambda$ .

**Fig.11** shows the direct comparisons between density profiles in different pores. It turns out the density profile inside a spherical pore **has** a more pronounced structure than that inside a slit pore. This is because the **spherical** pore involves more spatial hindrance than the slit pore.

In summary, compared with simulation the **PY/PY** approximation is the best approximation among the three approximations we studied in the slit-pore case, while the **HNC/PY** approximation is the best in the spherical-pore problem. Several earlier methods, which were used for improving the **PY/PY** approximation in the single-hard-wall problem [for example, renormalized HNC (RHNC), generalized mean spherical approximation (**GMSA**), exponential (EXP) **approximation**<sup>20</sup> and the **Plischke-Henderson method**<sup>21</sup>]] may be applicable here. It will be very interesting to see how good these are when generalized to the pore systems. However, more simulations are clearly needed for further comparisons.

## VI EXTENSIONS

There is **evidence**<sup>22</sup> that standard closures of the sort used in section V will not provide an adequate treatment of "surface" **phases** important to wetting phenomena that occur in **systems** in which the **molecular pair potential** and the **pore-molecule potential** have attractive terms. We briefly **outline** below an alternative closure **formalism** of a non-local density-functional form that may prove useful in **this** regard. It is based upon an expansion of the direct correlation function that was **introduced**<sup>23,24</sup> some time ago by one of us to study critical phenomena, and subsequently extended by Blum and **Stell**<sup>25</sup> to the wall problem and by Sullivan and **Stell**<sup>26</sup> to the two-phase interface problem. The wall-problem extension of Blum and **Stell** is immediately applicable to the pore problem except for trivial notational changes. Instead of (2.10), equation (44) of [24] yields

$$c_{mp}(r) = -\beta u_{mp}(r) - \beta \{ \mu_{\rho^*}(r) - \mu - \rho_m h_{mp}(r) \frac{\partial \mu}{\partial \rho_m} \} + \sum_{n \geq 1} S_n(r) \quad (6.1a)$$

Here

$$S_1(r_{12}) = \rho_m \int [h_{mp}(r_{13}) - h_{mp}(r_{12})] [\hat{c}(r_{23})_{\rho^*(12)} - \hat{c}(r_{23})] dr_3 \quad (6.1b)$$

and, for  $n \geq 2$ ,

$$S_n(r_{12}) = \frac{\rho_m^n}{n!} \int \prod_{i=2}^{n+1} [h_{mp}(r_{1i}) - h_{mp}(r_{12})] \hat{c}(2, \dots, n+2)_{\rho^*(12)} dr_3 \cdots dr_{n+2}, \quad (6.1c)$$

where  $\mu$  is the chemical potential of species  $m$ , and  $\mu_{\rho^*}(r)$  is  $\mu$  evaluated at  $\rho_m = \rho^*(r)$ , a function we **discuss** below. Also,

$$\hat{c}(r_{23}) = c(r_{23}) - \delta(r_{23})/\rho_m, \quad (6.1d)$$

$$\hat{c}(1, \dots, n)_{\rho^*(r_{ij})} = \frac{\delta^{n-2} \hat{c}(r_{12})}{\delta \rho(r_3) \cdots \delta \rho(r_n)} \Big|_{\rho^*(r_i) = \rho^*(r_{ij})} \quad (6.1e)$$

When  $\rho_m^*(r_i)$  is taken to be  $\rho_m$ , (6.1) reduces to a local **density-functional** expansion of  $c_{mp}(r)$  yielding an expansion that stands to the mean-spherical approximation as (2.10a) and (2.10b) stand to the PY and HNC approximations, respectively. The non-local analogs of (2.10a) and (2.10b) are obtained from (48) and (47) in ref.

[25]. In that reference,  $\rho^*(\mathbf{r})$  is taken to be  $\rho_m g_{mp}(\mathbf{r})$ . For asymptotic analysis this is a natural choice, but as a source of integral-equation closures, the choice is computationally awkward one, primarily because of the large rapidly-varying excursions from one that  $h_{mp}(\mathbf{r})$  can be expected to make as a function of  $\mathbf{r}$  for small  $\mathbf{r}$  and large  $\rho_m$ . Instead a smoothed weighted mean of  $g_{mp}(\mathbf{r})$  of the form

$$\rho^*(\mathbf{r}_{12}) = \int g_{pm}(\mathbf{r}_{12}) m(\mathbf{r}_{23}) d\mathbf{r}_3, \quad (6.2)$$

with  $m(\mathbf{r})$  an appropriate weight function, appears to be a much better choice. Perhaps the simplest choice appropriate to the problem at hand has already been considered by one of us as part of more general discussing of effective-density approaches<sup>19c</sup>. It yields the result [ Eq. (12-13) of ref. 19c ]

$$m(\mathbf{r}) = f(\mathbf{r}) / \int f(\mathbf{r}) d\mathbf{r} \quad (6.3)$$

where  $f(\mathbf{r})$  is the Mayer f-function,  $f(\mathbf{r}) + 1 = \exp[-\beta u_{mm}(\mathbf{r})]$ . A choice that is equivalent for hard spheres was subsequently considered by Tarazona<sup>27</sup> and Tarazona and Evans<sup>28</sup>. in the somewhat different context of a non-local density-functional theory for free-energy functionals. Other less simple choices were also discussed in ref. [19c] as well as in later work by Tarazona<sup>29</sup> and by Curtin and Ashcroft<sup>30</sup>. Their work is not in the integral-equation context we consider here, however. Further investigation will be needed to determine which choice yields best results for pore problems in the presence of attractive terms. For such problems an analogous non-local closure may well prove necessary in the determination of the bulk direct correlation function too.

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## REFERENCES

- 1** Evans, R. and Marconi, U. M. B., *J. Chem. Phys.*, **86**,7158 (1987).
- 2** (a) Post, A. J. and Glandt, E. D., *J. Colloid Interface Sci.*, **108**,31(1985).  
(b) Glandt, E. D., *J. Colloid Interface Sci.*, **77**,512 (1980).  
(c) Glandt, E. D., *AIChE J.*, **27**,51 (1981).  
(d) Post, J. J. *Coll. Int. Sci.* (in press) (1988).
- 3** McQuarrie, D. A. and Rowlinson, J. S. *Mole. Phys.*, **60**,977 (1987).
- 4** Macpherson, A. K., Carignan, Y. P., and Vladimiroff, T., *J. Chem. Phys.*, **87**, 1768 (1987).
- 5** Antonchenko, V. Y., Ilyin, V. V., Makovsky, N. N., Pavlov, A. N., and Sokhan, V. P., *Mole. Phys.* **62**, **345** (1984).
- 6** Schoen, M., Diestler, D. J., and Cushman, J. H. *J. Chem. Phys.*, **87**,5464 (1987).
- 7** MacElroy, J. M. D. and Sun, S-H, *Mole. Phys.*,**60**,475 (1987).
- 8** Peterson, B. K., and Gubbina, K. E., *Mole. Phys.*,**62**,215 (1987). See also Heffelfinger, G. S., Swol, F. V., and Gubbins, K. E., *Mole. Phys.*,**61**,1381 (1987).
- 9** Henderson, J. R., *Mole. Phys.*,**59**,89 (1986).
- 10** Freasier, B. L. and Nordholm, S. J. *J. Chem. Phys.*,**79**,4431 (1983).
- 11** Tarazona, P., and Vicente, L. *Mole. Phys.*,**56**,557 (1985).
- 12** Friedman, H. L., *A Course in Statistical Mechanics*, Prentice-Hall, Inc., Englewood Cliffs, New Jersey(1985).
- 13** Stell G., *Physica* **39**,517 (1965). The appendix of this article discusses the BBGKY hierarchy and its systematic closure.
- 14** See e.g. Fischer J., *Mole. Phys.* **33**, 75 (1977).
- 15** Losada-Cassou, M, *J. Chem. Phys.*, **80**,3344 (1984). Losada-Cassou, M. and Henderson, D. *Chem. Phys. Lett.*, **127**, 392 (1986).
- 16** Lebowitz, J. L., *Phys. Rev.*, **133**, A895(1964).
- 17** Henderson, D., Abraham, F. F. and Barker, J. A., *Mole. Phys.*, **31**,1291 (1975).



- 18 Giddings, J. G., Kucera, E., **Russell**, C. P., and Myers, M. N., *J. Phys. Chem.*, 72,4397 (1968).
- 19 (a) Enskog, D., *Kinetische Theorie der Vorgänge in mässig verdünnten Gasen, Diss.*, Uppsala. 1917.
- (b) **Singwi**, K.S., Tosi, **M.P.**, Land, R. H., and **Sjölander**, *Phys. Rev.*, 176,589 (1968).
- (c) see **section 12** of the article by G. **Stell** in *The Equilibrium Theory of Simple Fluids*, edited by H. L. **Frisch** and J. L. **Lebowitz**. Benjamin N.Y. 1964.
- 20 Sullivan, D. E. and **Stell**, G. *J. Chem. Phys.*, 69,5450 (1978).
- Sullivan, D. E., **Levesque**, D. and **Weis**, J. J. *J. Chem. Phys.*, 72,1170 (1980).
- 21 **Plischke**, M. and Henderson, D. *J. Chem. Phys.*, 84,2846 (1986).
- 22 Evan, R, Tarasona, P., and **Marini Bettolo Marconi**, U., *Mol. Phys.* 50, 993 (1983).
- 23 **Stell**, G., *Phys. Rev. Lett* **20**, 553 (1968). A non-local density-functional expansion of the direct correlation function was also used to obtain an integral equation for an approximate radial distribution function in a contributed paper by J. K. **Percus** and G. **Stell**, *IUPAP Conf., Aachen*, Germany, June 18, 1964.
- 24 **Stell**, G., *Phys. Rev. B* 2, 2811 (1970).
- 25 Blum, L. and **Stell**, G., *J. Stat. Phys.*, **15**,459(1976).
- 26 Sullivan, D. and **Stell**, G., *J. Chem. Phys.* 67,2567 (1977).
- 27 Tarasona, P., *Mol. Phys.* **52**, 81 (1984).
- 28 Tarasona, P., and Evans, R., *Mol. Phys.* **52**, 847 (1984).
- 29 Tarasona, P., *Phys. Rev. A* S1, 2672 (1985).
- 30 Curtin, W. A. and **Ashcroft**, N. W., *Phys. Rev. A* **32**, 2909 (1985).

## Figure Captions

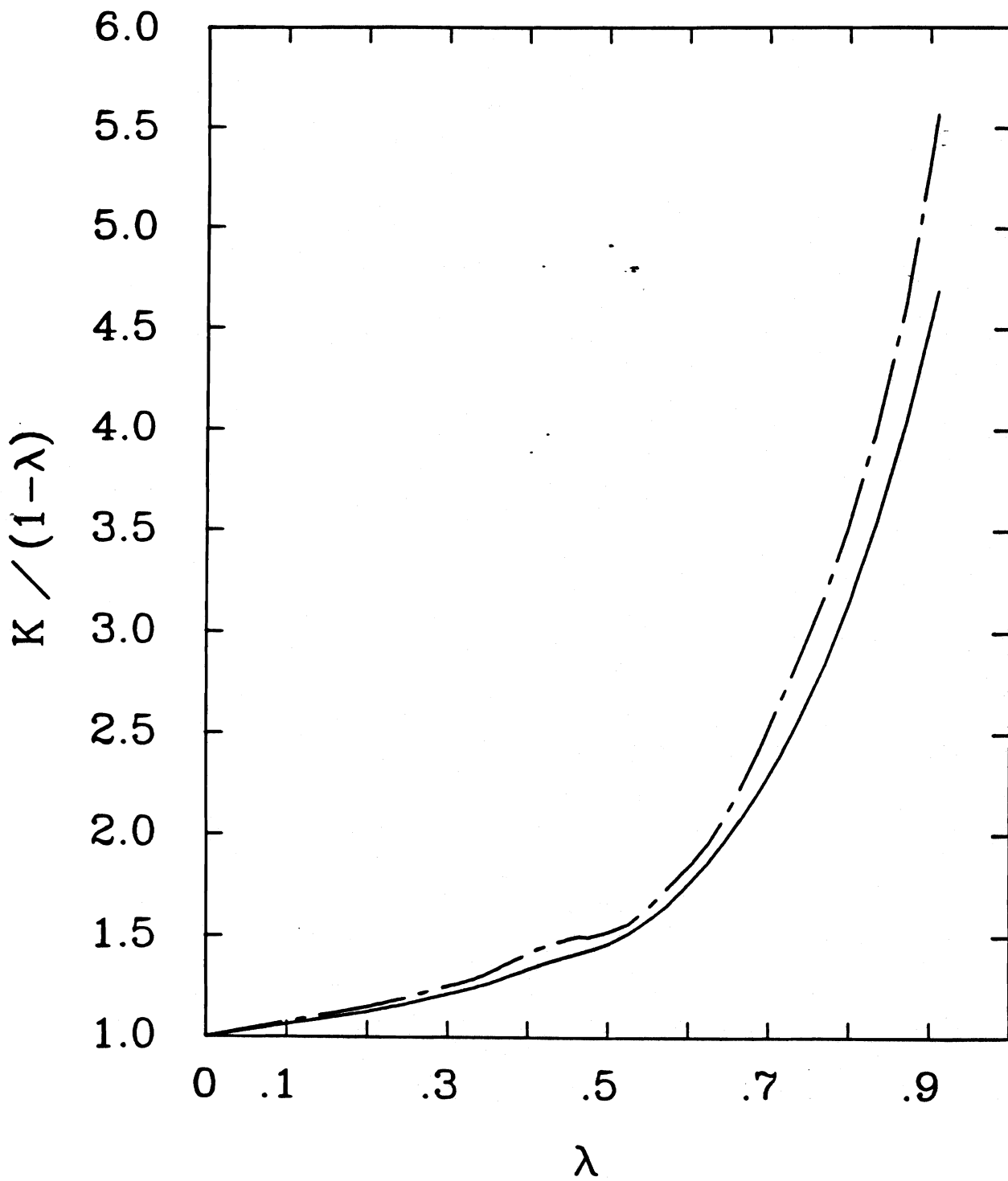
- Fig.1** The partition coefficient,  $K/K_0$ , for a slit pore as a function of the diameter ratio,  $\lambda (= \frac{d_p}{d_m})$ , at reduced bulk densities  $\rho_m d_m^3 = 0.5$ . The **PY/PY** approximation (—), the **BBGKY-SA** (— · —).
- Fig.2** The partition coefficient,  $K$ , for a slit pore as a function of the reduced density,  $\rho_m d_m^3$ , at different diameter ratios. From lower to upper sets of curves  $\lambda = 0.5, 0.25$ . Other symbols as in **Fig.1**.
- Fig.3** The reduced pressure acting on the wall,  $\beta P^W d_m^3$ , as a function of  $(L - d_m)/d_m$  at a fixed reduced density  $\rho_m d_m^3 = 0.5$ . **Simulation** results<sup>S</sup> (•). Straight line: the reduced bulk pressure,  $\beta p^B d_m^3$ . Other symbols as in **Fig.1**.
- Fig.4** The reduced solvation force ( $f/p^B$ ) for a slit pore as a function of the reduced density,  $\rho_m d_m^3$ . From lower to upper sets of curves at  $\rho_m d_m^3 = 0.6$ ,  $\lambda = 0.25, 0.5$ . Other symbols as in **Fig.1**.
- Fig.5** The density profile,  $\rho_m(z) d_m^3$ , inside a slit pore as a function distance,  $z/(L/2 - R_m)$ . The **PY/PY** approximation (—), the **HNC/PY** approximation (- · -) and the **BBGKY-SA** (— · —). Simulations of ref. **5**(•).
- $\rho_m d_m^3 = 0.5$ ,  $\lambda = 111.5$
  - $\rho_m d_m^3 = 0.5$ ,  $\lambda = 1/2.0$
  - $\rho_m d_m^3 = 0.5$ ,  $\lambda = 1/3$
  - $\rho_m d_m^3 = 0.5$ ,  $\lambda = 1/4.78$
  - $\rho_m d_m^3 = 0.5$ ,  $\lambda = 1/5.5$
- Fig.6** The partition coefficient,  $K/K_0$ , for a spherical pore as a function of the diameter ratio,  $\lambda (= \frac{d_p}{d_m})$ .  $\rho_m d_m^3 = 0.5$ , Other symbols as in **Fig.5**.
- Fig.7** The partition coefficient,  $K$  for a spherical pore as a function of the reduced density,  $\rho_m d_m^3$ , at different diameter ratios. From lower to upper sets of curves,  $\lambda = 0.5, 0.25$ . Other symbols as in **Fig.5**.
- Fig.8** The reduced solvation force,  $f/[p^B(1 - \lambda)^2]$ , for a spherical pore as a function of the diameter ratio  $\lambda$ .  $\rho_m d_m^3 = 0.5$ . Other symbols as in **Fig.5**.

Fig.9 The reduced solvation force,  $f/p^B$ , for a spherical pore as a function of the reduced density,  $\rho_m d_m^3$ . From lower to upper sets of curves  $\lambda = 0.5, 0.25$  respectively. Other symbols as in Fig.5.

Fig.10 The density profile,  $g_{mp}(r)$ , for a spherical pore as a function of distance,  $r/d_m$ . In fig.10f, simulation data<sup>6</sup>(•). Other symbols as in Fig.5.

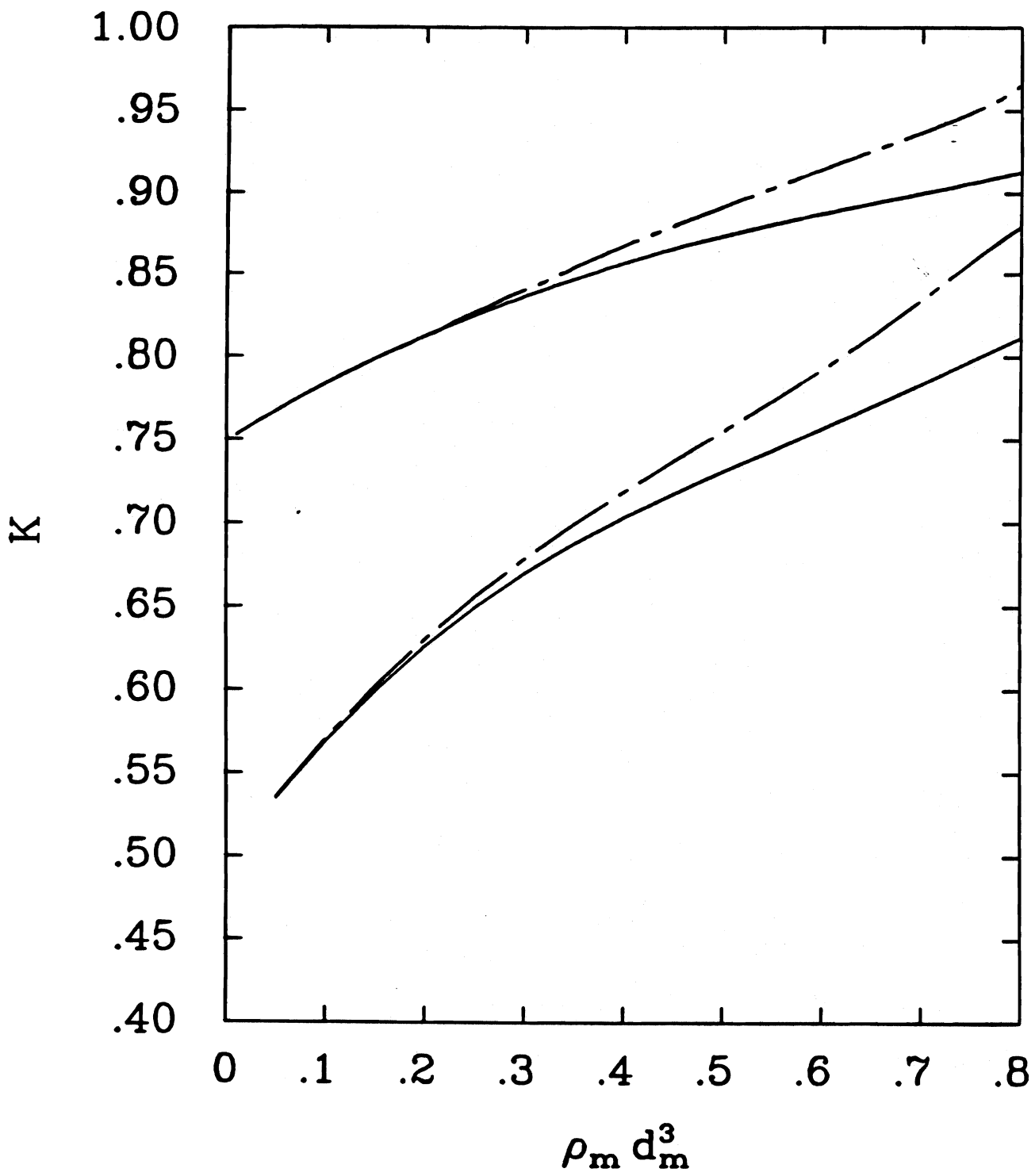
- a.  $\rho_m d_m^3 = 0.5, \lambda = 1/2$
- b.  $\rho_m d_m^3 = 0.5, \lambda = 1/3$
- c.  $\rho_m d_m^3 = 0.5, \lambda = 1/4$
- d.  $\rho_m d_m^3 = 0.5, \lambda = 1/5$
- e.  $\rho_m d_m^3 = 0.5, \lambda = 1/10$
- f.  $\rho_m d_m^3 = 0.86, \lambda = 1/13$

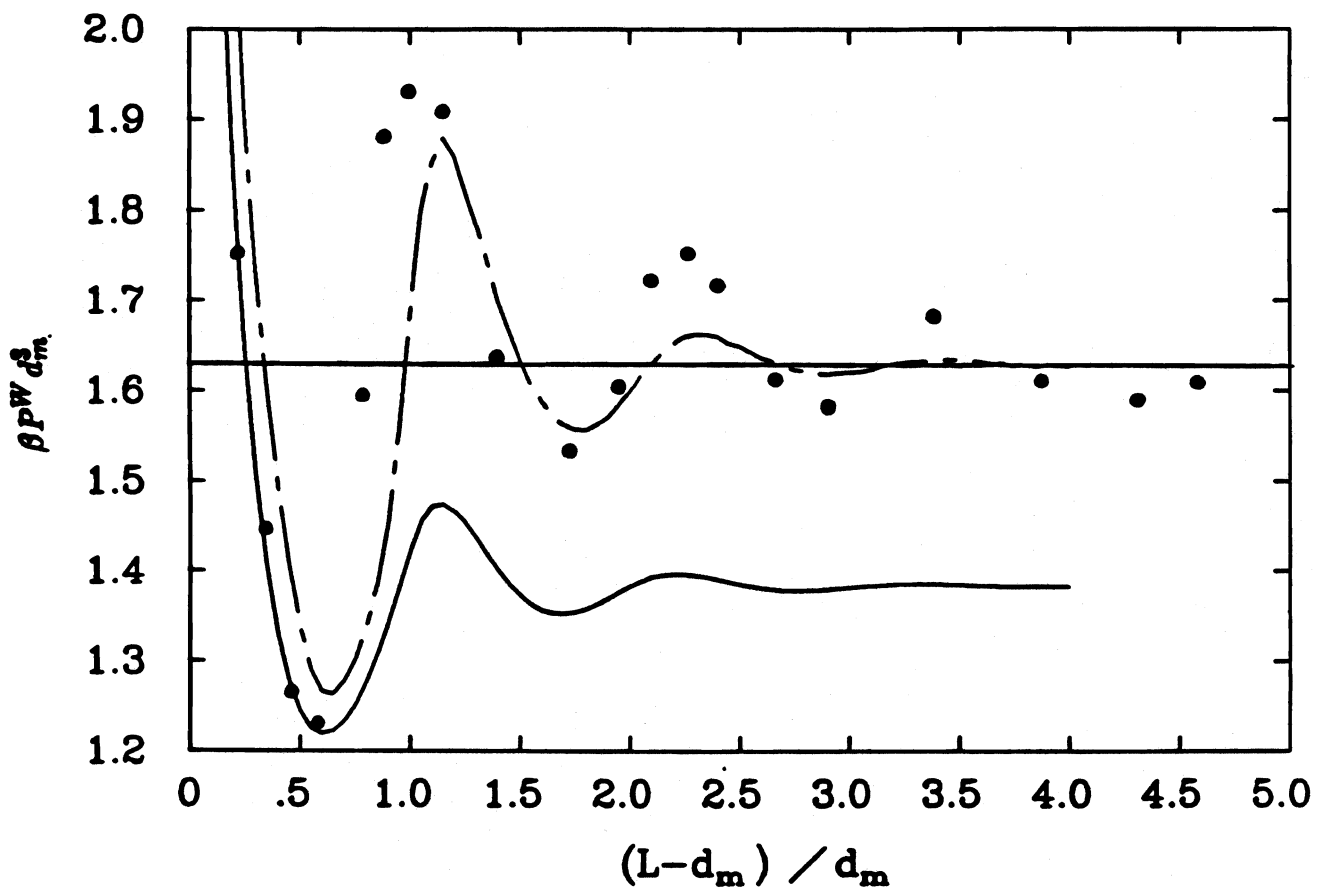
Fig.11 The density profile inside slit and spherical pores.  $\rho_m d_m^3 = 0.5, \lambda = 1/5.5$   
 The solid line: the PY/PY result in a slit-pore problem, dashed line: the HNC/PY result in a spherical-pore problem.

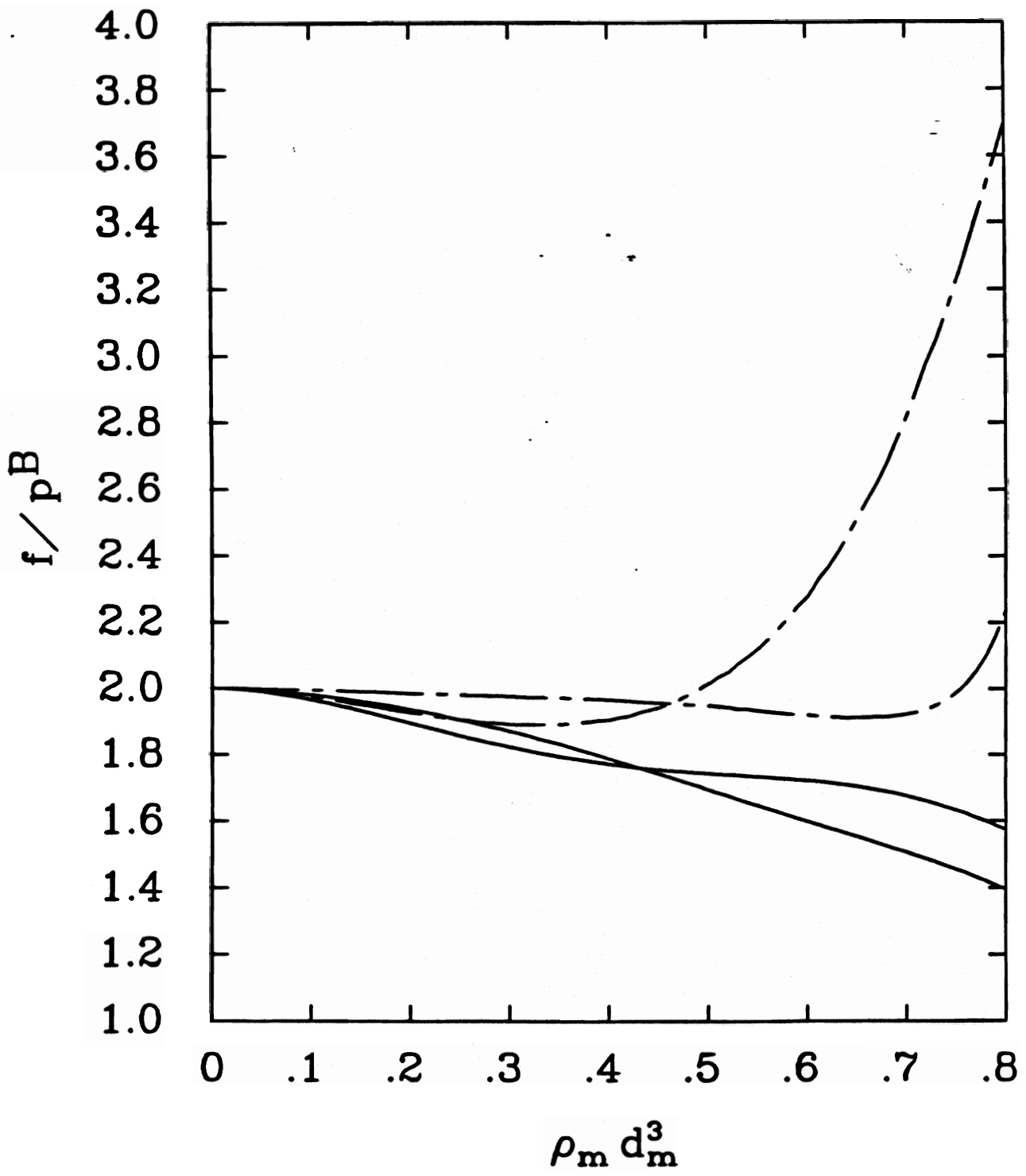


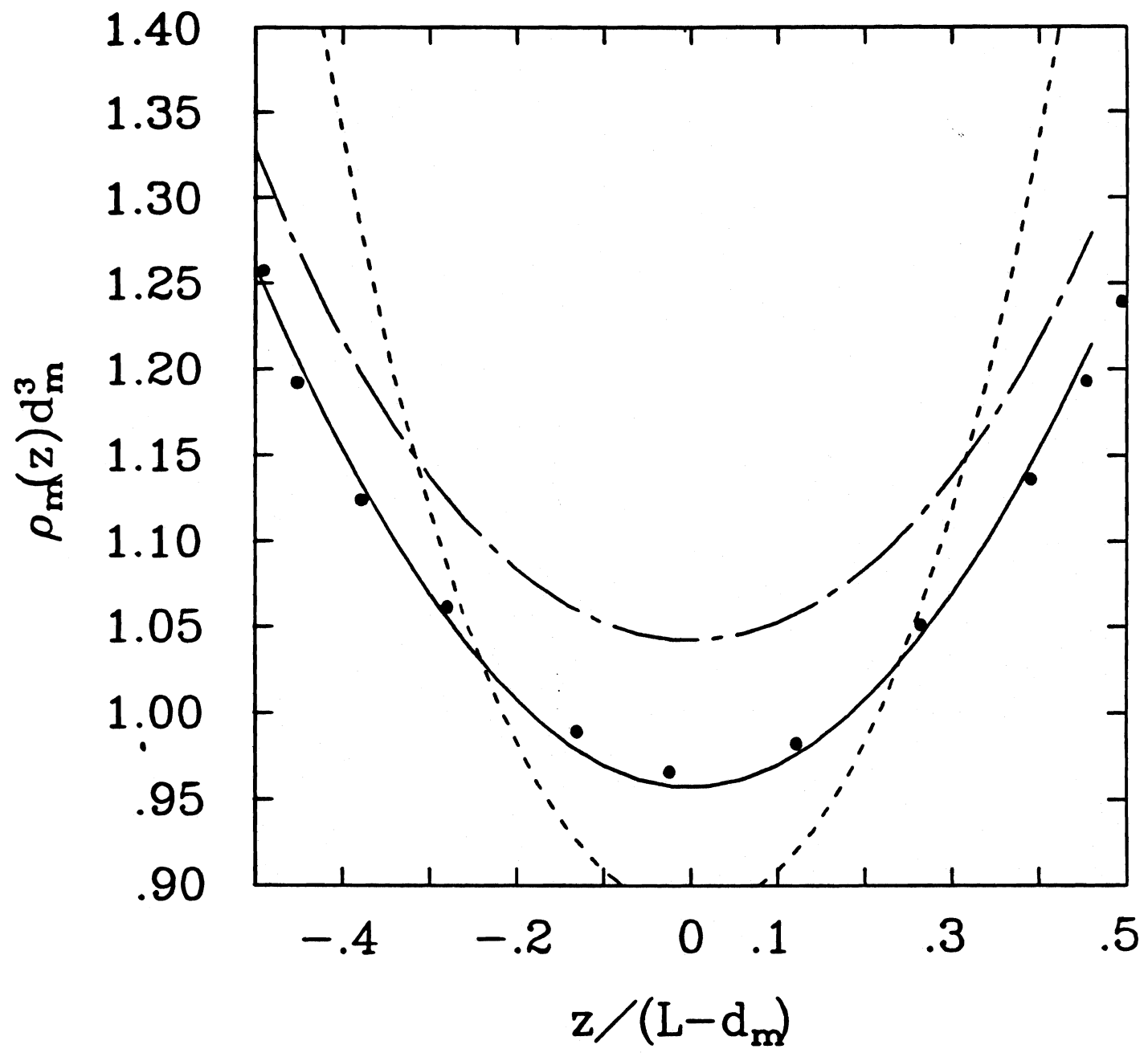
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Fig.1

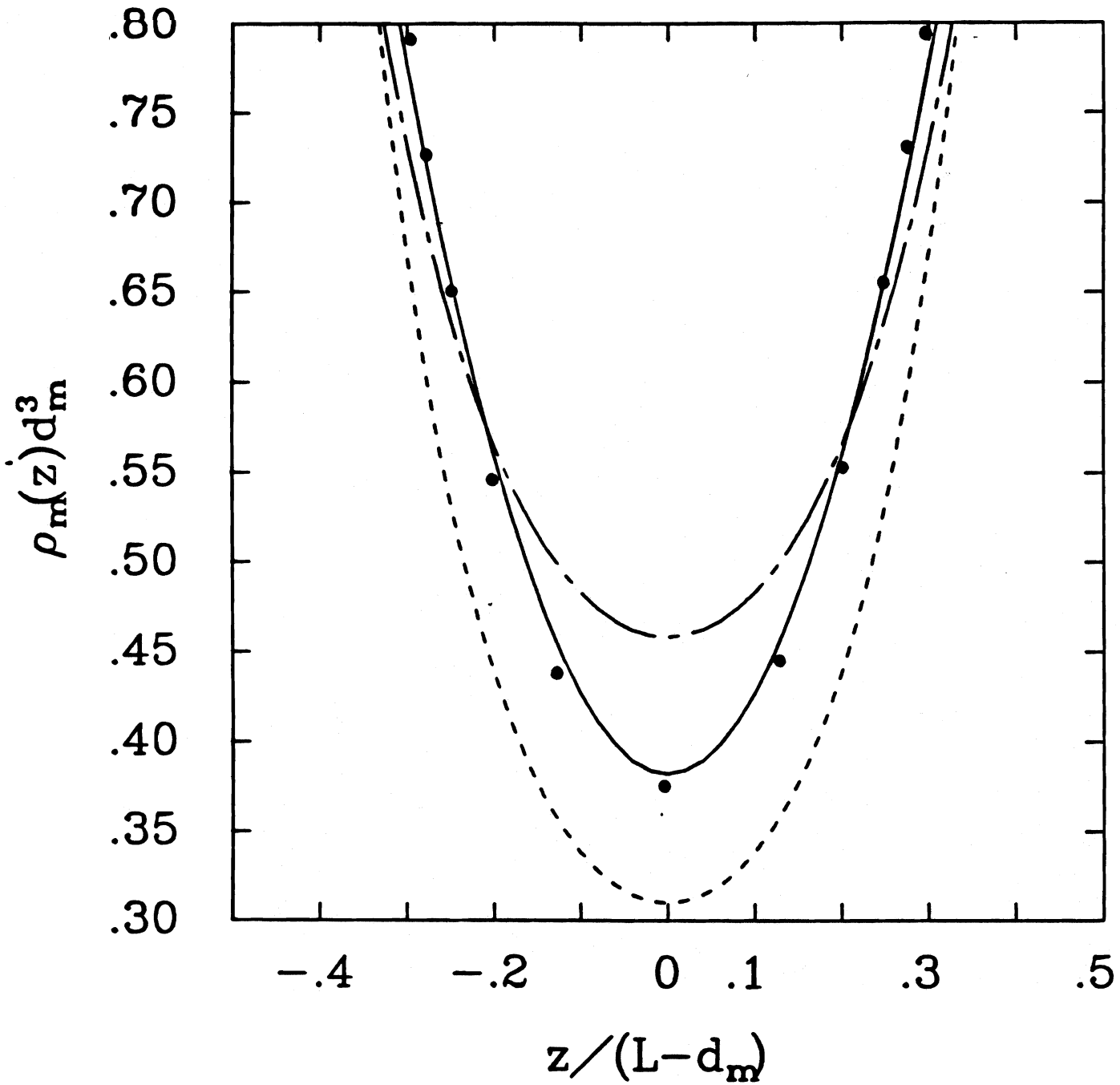


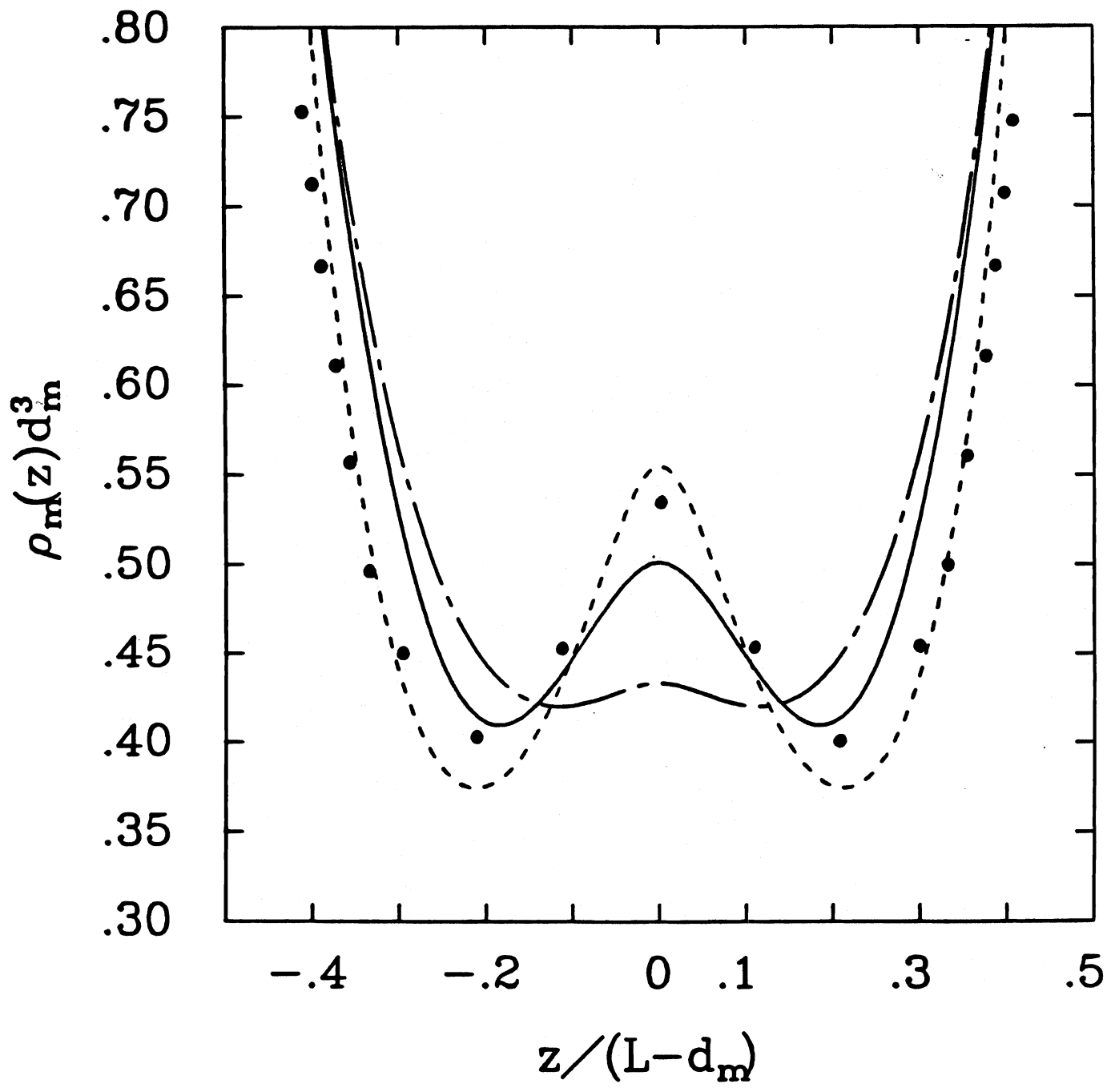


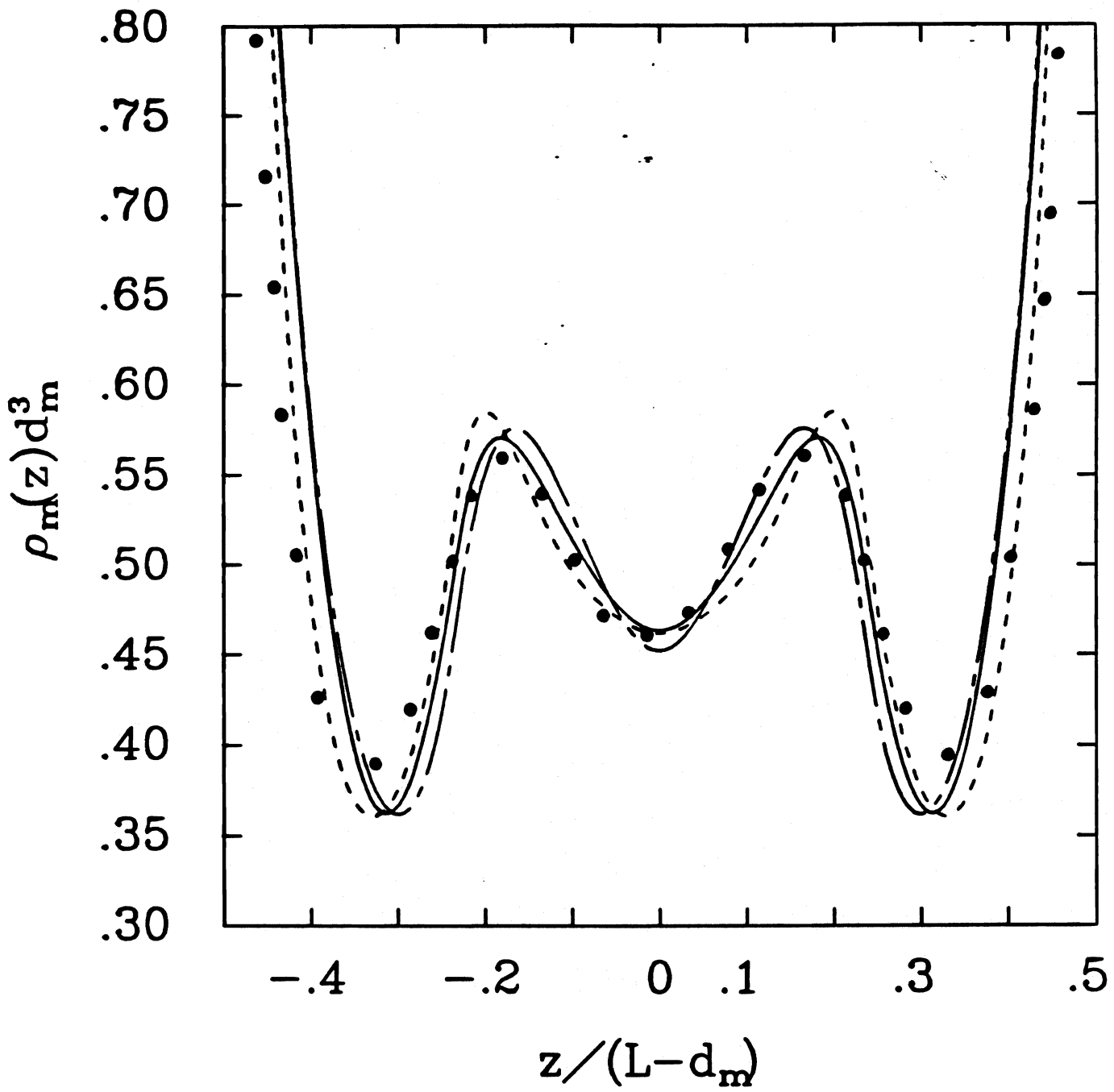


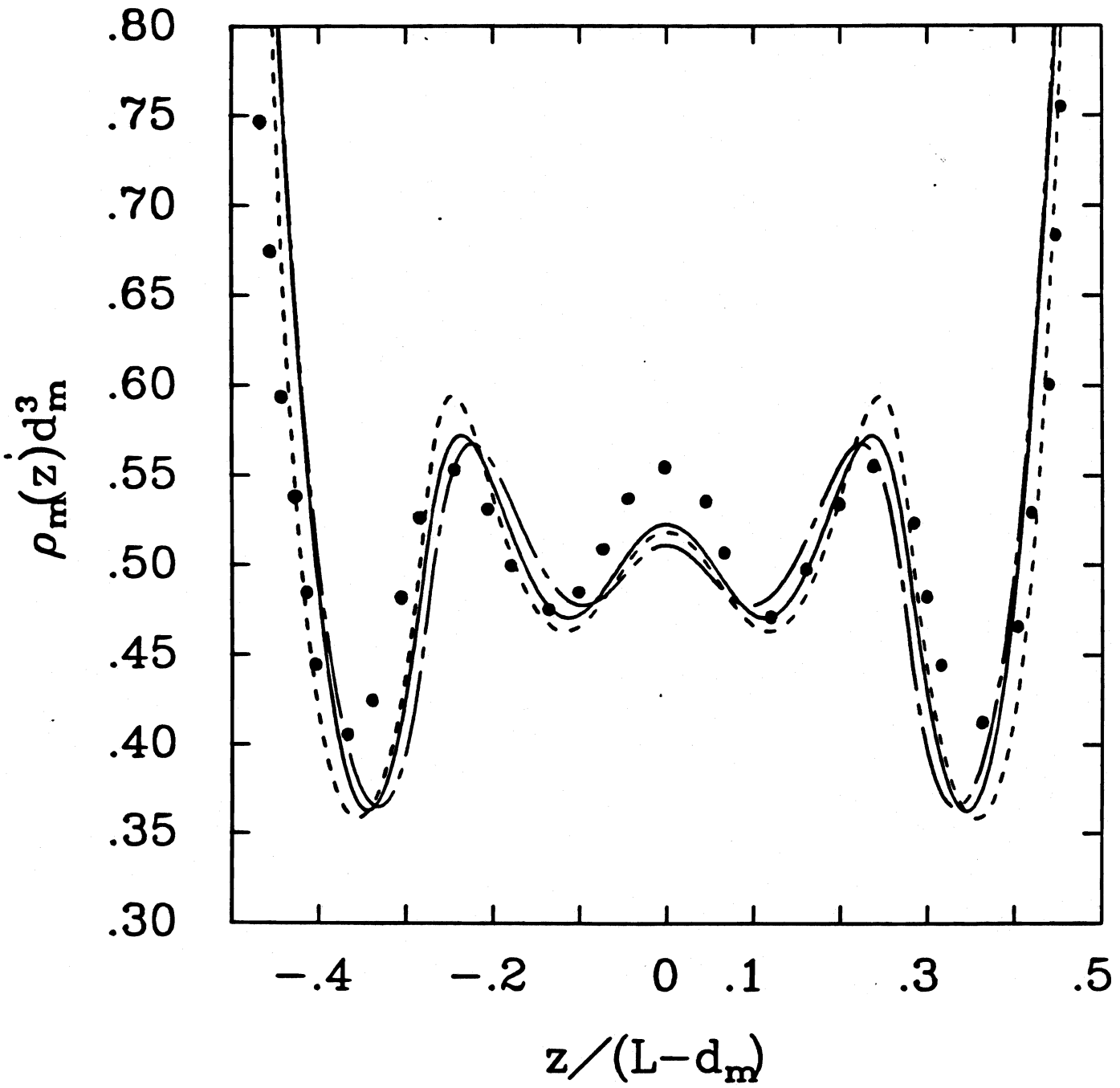


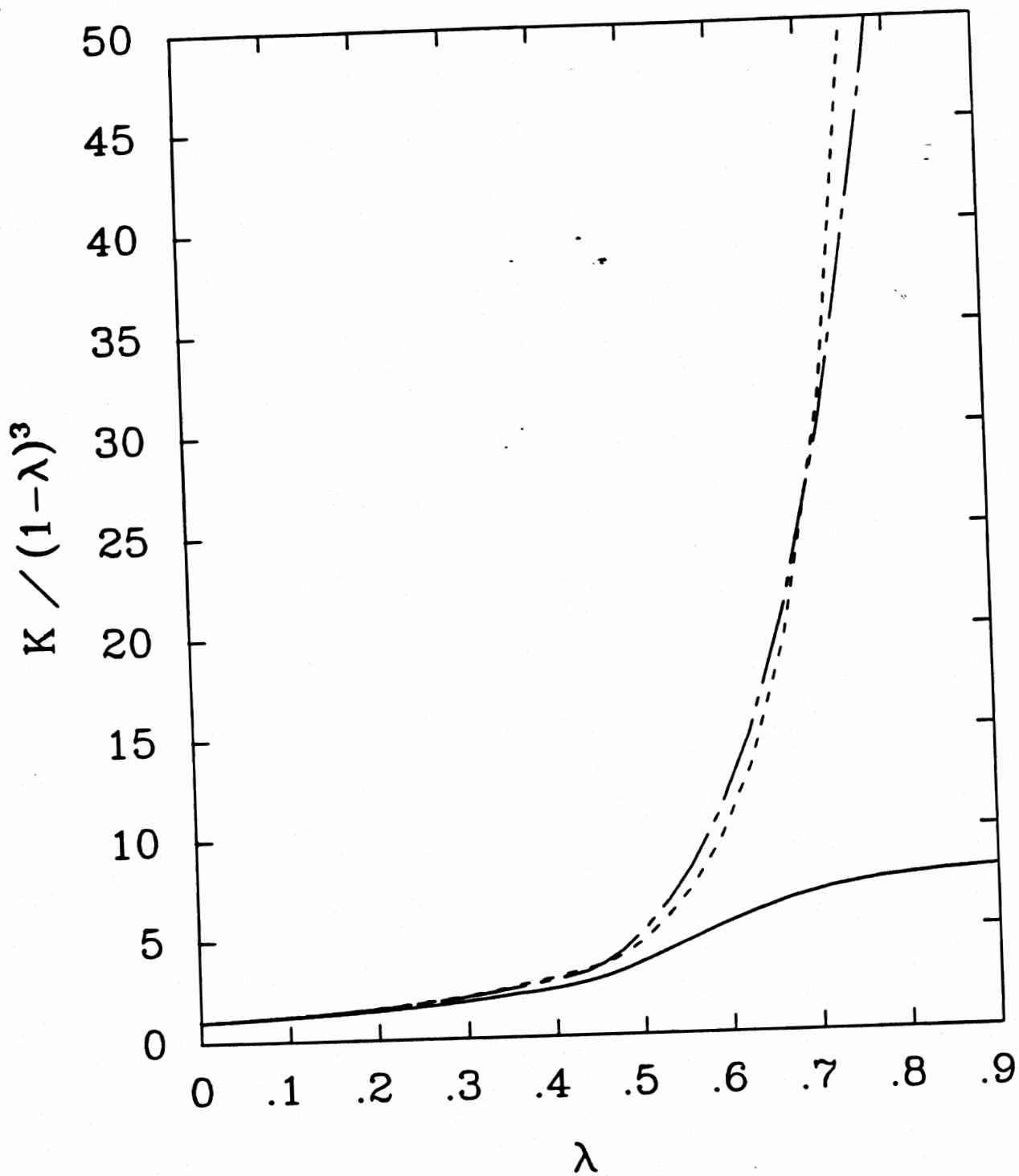


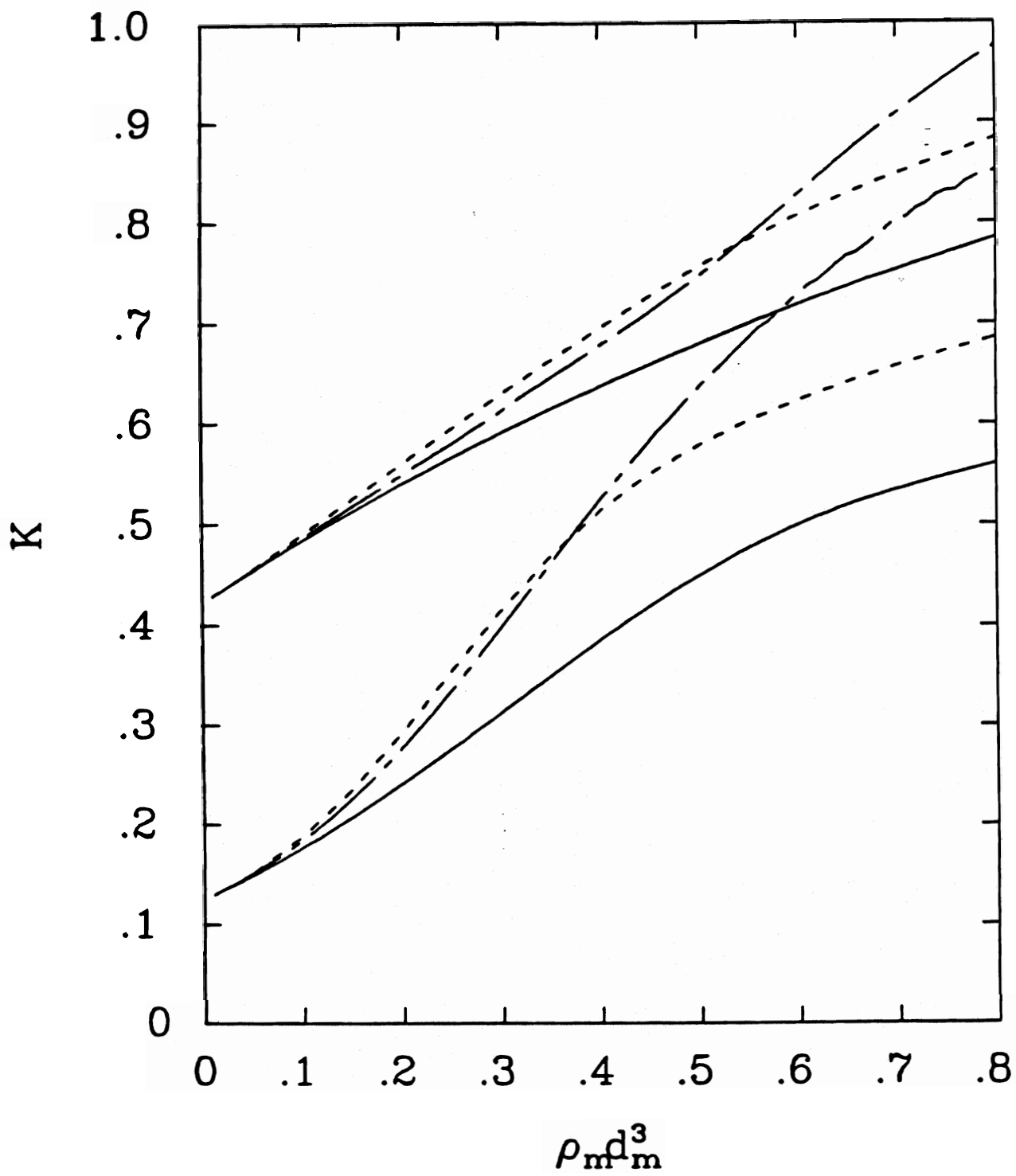












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Fig.?

