

## Classical fluid structure near solid substrates: A comparison of different theories

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Different approximate analytical theories for dealing with nonuniform classical fluids are compared as approximations to a formally exact theory. The focus is on the situation where the nonuniformities are due to the interaction of the fluid with a model solid substrate. Detailed calculations are made using a density-functional theory previously developed by the authors, and a theory of a type used in a number of recent calculations, in which the perturbation caused by the fluid is dealt with using the Percus-Yevick (PY) approximation. Both theories use the PY approximation to treat pair correlations in the fluid. The density-functional theory turns out to be markedly the superior of the two for the case where the substrate should produce an unsaturated liquid film near the fluid-substrate interface. The density-functional theory correctly predicts the presence of such a film, whereas the other theory, essentially because it treats the response to the substrate perturbation linearly, yields no film. Microscopically detailed fluid-density profiles are given for both theories.

### I. INTRODUCTION

In recent years the problem of calculating the detailed microscopic structure of simple fluids near model solid substrates has received a considerable amount of attention. The treatments fall into the usual classes, those based on approximate analytical theories<sup>1-7</sup> and those utilizing computer simulations.<sup>5,8</sup> We shall focus primarily upon the analytical work in this paper.

The analytical theories are best viewed in the context of a formally exact theory for a simple one-component fluid having equilibrium density  $n(\vec{r})$  in the presence of an external perturbing potential  $V(\vec{r})$ . In the *exact* theory<sup>9</sup>

$$n(\vec{r}) = n_0 e^{-\beta V(\vec{r})} \times \exp\left(\int_0^1 d\alpha \int d^3r' c(\vec{r}, \vec{r}'; \alpha) [n(\vec{r}') - n_0]\right). \quad (1)$$

Here  $\beta = 1/kT$ ,  $n_0$  is the density in the absence of (or far away from) the perturbation, and  $c(\vec{r}, \vec{r}'; \alpha)$  is the exact direct correlation function for a particular value of  $\alpha$ , a parameter characterizing the degree to which the perturbation is turned on. ( $\alpha$  is explicitly defined in Ref. 9.)

The approximate analytical theories fall into two categories. The first category consists of theories which utilize at the outset an idea originally due to Helfand, Frisch, and Lebowitz.<sup>10</sup> In this approach one considers a binary fluid formed from atoms of types *A* and *B* in which the concentration of one of the components, labeled *A*, tends toward

zero while the size of the *A* atoms tends toward infinity. In this limit the outer edge of an *A* atom becomes a planar wall seen by the *B* atoms. The Ornstein-Zernicke equation for the *AB* correlation functions becomes

$$h_{AB}(\vec{r} - \vec{r}') = c_{AB}(\vec{r} - \vec{r}') + n_B^0 \int d^3r'' h_{AB}(\vec{r} - \vec{r}'') c_{AB}(\vec{r}'' - \vec{r}'), \quad (2)$$

where  $c_{ij}$  ( $i, j = A, B$ ) is a direct correlation function,  $n_B^0$  is the average number density of *B* atoms, and  $g_{ij} = 1 + h_{ij}$  is a pair-correlation function. The spatially varying density of *B* atoms near the wall is just

$$n_B(\vec{r}) = n_B^0 g_{AB}(\vec{r}) \quad (3)$$

for an *A* atom located at  $\vec{r} = 0$ . If one takes  $c_{BB}$  as being given and relates  $c_{AB}$  to  $h_{AB}$  by some approximate theory, e.g., the Percus-Yevick (PY) theory, (2) becomes a linear integral equation easily solved by numerical methods. It is useful to combine (2), (3), and the PY equation

$$c_{AB}(\vec{r}) = g_{AB}(\vec{r}) (1 - e^{\beta V_{AB}(\vec{r})}) \quad (4)$$

to obtain

$$n_B(\vec{r}) = n_B^0 e^{-\beta V_{AB}(\vec{r})} \times \left(1 + \int d^3r' c_{BB}(\vec{r} - \vec{r}') [n_B(\vec{r}') - n_B^0]\right). \quad (5)$$

Equation (5) or its equivalent has been used recently by a number of authors. Perram and White<sup>1</sup> have used it to compute  $n_B(\vec{r})$  for the case where

the  $B$  atoms are hard spheres and the  $A$  atom is a large hard sphere located at  $\vec{r}=0$ ; when the  $A$  atom is sufficiently large its surface, of course, is essentially a planar wall as viewed by the  $B$  atoms. Henderson, Abraham, and Barker<sup>2</sup> have performed the same calculation in the limit that the  $A$ -atom radius tends to infinity, its surface remaining at  $z=0$ . Waisman, Henderson, and Lebowitz<sup>3</sup> have treated the more general case where the hard-sphere potential of the  $A$  atom has a Yukawa tail tacked onto it and the mean spherical approximation is made in arriving at the solution for  $n_B(\vec{r})$ . Fischer<sup>4</sup> has begun with (2) and compared results of combining it with the PY and superposition approximations for hard-sphere particles against a hard wall. Very recently Abraham and Singh<sup>5</sup> have used the results of Ref. 3, viewed as a corrected PY theory for hard spheres against a hard wall, to deal with the effects of a (9-3) interaction between the hard spheres and the wall; the (9-3) interaction<sup>11</sup> is dealt with using the Anderson-Weeks-Chandler perturbation theory.<sup>12</sup>

The nature of the approximations inherent in (5) becomes evident when it is compared with the exact result (1). In fact, it is easy to see that (5) is obtained from (1) by expanding the exponential involving  $c$  and retaining only the term *linear* in the density deviations. In this case,  $c$  is taken to be that appropriate to a uniform system having density  $n_0=n_B^0$ , and the integral over  $\alpha$  gives simply a factor of unity. This approximation is, of course, just the PY approximation for the correlations induced by  $V(\vec{r})$ . In what follows we shall therefore refer to the theories just discussed<sup>13</sup> as linear PY (LPY) theories.

The second category of theory, known as density-functional theory, has recently been most fully developed by Ebner, Saam, and Stroud<sup>6</sup> and Saam and Ebner.<sup>9</sup> For brevity we refer to this theory as ESS theory. Earlier references may be found in Ref. 6. In essence ESS minimize a free energy, a procedure in principle equivalent<sup>9</sup> to solving (1), using the approximation that

$$2 \int_0^1 d\alpha \int_0^\alpha d\alpha' c(\vec{r}, \vec{r}'; \alpha') = c(\vec{r} - \vec{r}'; \bar{n}), \quad (6)$$

where  $c(\vec{r} - \vec{r}'; \bar{n})$  is the direct correlation function for a uniform fluid (the  $B$  fluid of the LPY theory) at density  $\bar{n}$  with  $\bar{n}$  given by the physically reasonable nonlocal form

$$\bar{n} = \frac{1}{2}[n(\vec{r}) + n(\vec{r}')]. \quad (7)$$

Ebner, Saam, and Stroud do *not* make a linear approximation for the correlations induced by  $V(\vec{r})$ . Further,  $c$  is not simply replaced by that appropriate to the unperturbed system. The approximation stated in (6) and (7) accounts in an approxi-

mate, but reasonable, way for the exact effects of the coupling constant integrations over  $\alpha$ . Since ESS actually calculate the right-hand side of (6) using the PY approximation for a system at density  $\bar{n}$ , their final result is best viewed in the light of the much more precise theory described in Ref. 9, where the fluid is dealt with using the PY approximation for a nonuniform system following which the effects of the perturbation are dealt with exactly. The ESS theory thus includes in a non-trivial fashion both the PY for a nonuniform system and the nonlinear response of the system to the density deviations induced by turning on  $V(\vec{r})$ . *Neither* of these effects is included in the LPY theory. Consequently, LPY theory is expected to be significantly inferior to the ESS theory when  $V(\vec{r})$  represents a massive perturbation on the fluid system in question. In Sec. II we present the results of both theories for the case where  $V(\vec{r})$  is that due to a smoothed planar wall composed of atoms which interact with the fluid atoms via a Lennard-Jones (6-12) potential. We shall see that such a wall can in fact represent a massive perturbation on the system. In the case where an unsaturated film should form on the wall, the ESS theory is correct in that it predicts the existence and growth of such a film, whereas (4) fails miserably in that it predicts no film whatsoever. Section III is devoted to a summary and further discussion of our results.

## II. CALCULATIONS AND COMPARISONS

We begin with the linearized theory represented by (2)–(5). For computational purposes we have replaced (2) by the equivalent form

$$h_{AB}(\vec{r} - \vec{r}') = c_{AB}(\vec{r} - \vec{r}') + n_B^0 \int d^3r'' c_{AB}(\vec{r} - \vec{r}'') h_{BB}(\vec{r}'' - \vec{r}'). \quad (8)$$

Use of (2), (3), and the definition

$$y(\vec{r}) = g_{AB}(\vec{r}) e^{\beta V_{AB}(\vec{r})} \quad (9)$$

leads to

$$y(\vec{r}) = 1 + n_B^0 \int d^3r' y(\vec{r}') (e^{-\beta V_{AB}(\vec{r}')} - 1) h_{BB}(\vec{r}' - \vec{r}). \quad (10)$$

In the case where the  $A$  particle becomes very large, its surface remaining at  $z=0$  to produce a potential

$$V(z) = \begin{cases} \infty, & z < 0 \\ 4\pi \epsilon_{0w} n_w \sigma_w^3 \left[ \frac{1}{45} \left( \frac{\sigma_w}{z} \right)^9 - \frac{1}{6} \left( \frac{\sigma_w}{z} \right)^3 \right], & z \geq 0, \end{cases} \quad (11)$$

Eq. (10) takes the form

$$y(z) = 1 + n_B^0 \int_{-\infty}^{\infty} dz' y(z') (e^{-\beta V(z')} - 1) \times h_{BB}^0(z' - z), \quad (12)$$

where

$$h_{BB}^0(z' - z) = \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dy h_{BB}(\vec{r}' - \vec{r}). \quad (13)$$

The form of  $V(z)$  in (11) results from summing the effects of a continuum of atoms of density  $n_w$  located at  $z < 0$  and interacting with the fluid atoms at  $z > 0$  via a Lennard-Jones (6-12) potential characterized by range and depth parameters  $\sigma_w$  and  $\epsilon_{0w}$ . The  $B$  atoms are taken to be argon atoms for which we already have computed  $h_{BB}$  in the PY approximation.<sup>6</sup> In this paper we choose<sup>14</sup>  $\sigma_w = 3.727 \text{ \AA}$ ,  $\epsilon_{0w}/k = 153 \text{ K}$ , and  $n_w \sigma_w^3 = 0.988$ , parameters appropriate to a solid  $\text{CO}_2$  wall.

Solution of (11) and (12) is a reasonably straightforward numerical problem, some details of which are presented in Appendix A. In Fig. 1 we present results for the density profile

$$n(z) = y(z) n_B^0 e^{-\beta V(z)} \quad (14)$$

at  $T = 1.1$ . We use units of  $\sigma = 3.405 \text{ \AA}$  for length,  $\sigma^{-3}$  for density, and  $\epsilon_0/k = 119.76 \text{ K}$  for  $T$ ,  $\sigma$  and  $\epsilon_0$  being the 6-12 potential parameters for the argon-argon interaction. The liquid-gas critical temperature (in the PY approximation) is  $T_c = 1.32$  in these units. In Fig. 1 the asymptotic densities  $n_B^0$  are all less than the density under vapor pressure  $n_{vp}(T) = 0.04736$ . Note that there is absolutely no evidence of unsaturated film formation or growth. These results contrast sharply with those of the ESS theory,<sup>15</sup> shown in Fig. 2, for the same  $T$  and the same sequence of asymptotic densities plus one additional density. Here, we observe clear

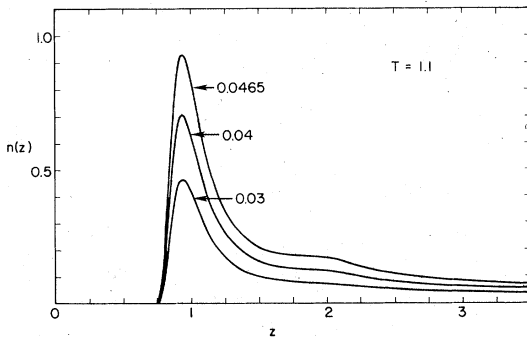


FIG. 1. Argon density profiles from the LPY theory at  $T = 1.1$  for values of  $n_B^0 = 0.030, 0.040, \text{ and } 0.0465$ . Reduced units, explained in the text, are used.

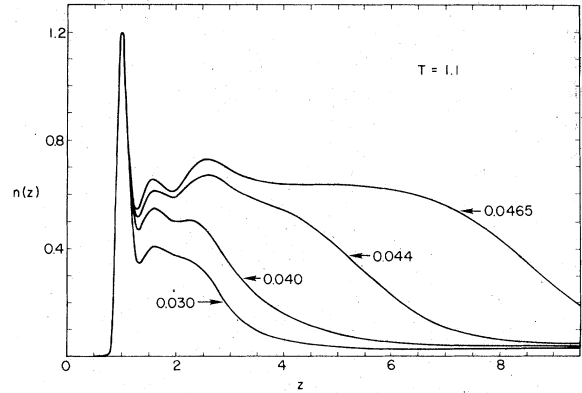


FIG. 2. Argon density profiles from the ESS theory at  $T = 1.1$  for values of  $n_B^0 = 0.030, 0.040, 0.044, \text{ and } 0.0465$ . Reduced units, explained in the text, are used. Film formation and growth is clearly visible here.

film formation and growth with increasing  $n_B^0$ . For the largest density  $n_B^0 = 0.0465$ , the film is particularly well defined, having a thickness of approximately eight layers. Computational details for the ESS theory are given in Appendix B.

It is also of interest to present some results for a temperature  $T = 1.4 > T_c$ . Here one has no film growth and one can clearly compare the predictions of the two theories as regards the profiles near the wall. The density sequence  $n_B^0 = 0.2, 0.3, 0.5$  is displayed in Figs. 3-5, the results of both theories for a given  $n_B^0$  appearing on a single figure.

There are several features worth pointing out. First, for the asymptotic densities 0.2 and 0.3, the density  $n(z)$  for the linear theory settles down to its asymptotic value considerably less rapidly than that for the ESS theory. This is because  $n_B^0 = 0.2$  and 0.3, for  $T = 1.4$ , are rather near the crit-

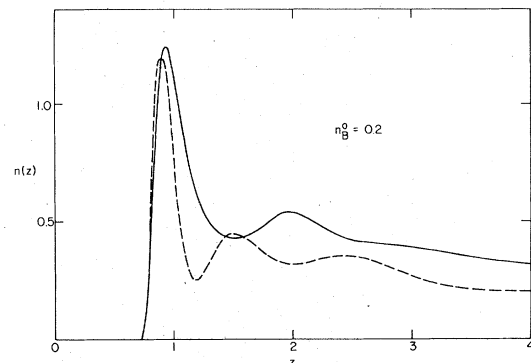


FIG. 3. Argon density profiles for the LPY theory (solid line) and ESS theory (dashed line) at  $T = 1.4$  and  $n_B^0 = 0.2$ . Reduced units, explained in the text, are used.

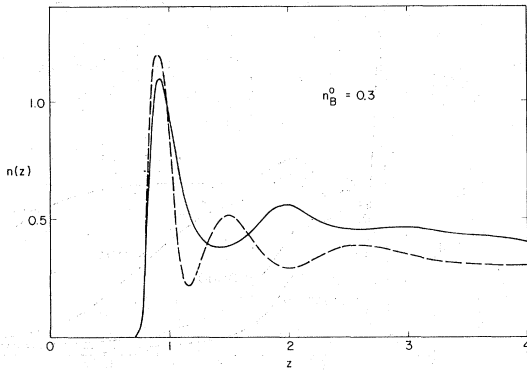


FIG. 4. Argon density profiles for the LPY theory (solid line) and ESS theory (dashed line) at  $T=1.4$  and  $n_B^0=0.3$ . Reduced units, explained in the text, are used.

ical point for argon (in the PY approximation). The linear theory uses correlation functions for the asymptotic density, whereas the ESS theory, by virtue of (6) and (7), uses correlation functions which sample a range of densities, some near the critical density and some farther away, the net effect being a relative shortening of the long-range correlations induced by the wall. This shortening is expected on obvious physical grounds. As seen in Fig. 5, the effect becomes small for  $n_B^0$  farther from the critical point.<sup>16</sup> Secondly, the oscillations in  $n(z)$  beyond the peak nearest the wall are different for the two theories in terms of relative phase. The dephasing effect occurs for the most part just beyond the first peak, where  $n(z)$  for the ESS theory falls to its first minimum and rises to its second maximum more rapidly than that for the linear theory. Again, this can be viewed as a consequence of the use of correlation functions corresponding to different densities in the two theories. The linear theory uses correlation func-

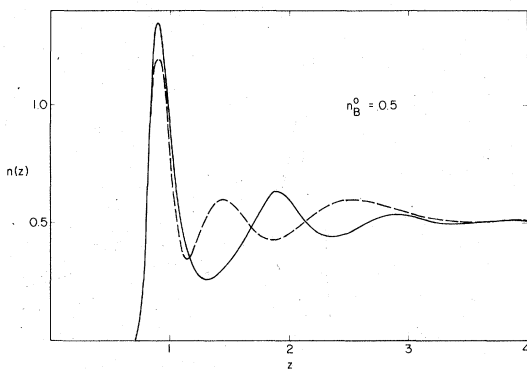


FIG. 5. Argon density profiles for the LPY theory (solid line) and ESS theory (dashed line) at  $T=1.4$  and  $n_B^0=0.5$ . Reduced units, explained in the text, are used.

tions for a lower density fluid near the walls than does the ESS theory.

### III. DISCUSSION

The essential point made in this paper is that LPY theories for classical fluids are incapable of handling large perturbations such as those leading to the formation and growth of unsaturated films on solid substrates; there are important nonlinear effects which must be dealt with and which, indeed, can be dealt with within the framework of the more sophisticated ESS theory. The real problem with the LPY theories in such a situation is that they treat correlations in the fluid using correlation functions appropriate to the vapor phase far from the substrate, whereas the construction of the unsaturated film requires a theory which uses correlation functions containing information about local densities, as does ESS theory.

It would be of considerable interest to test the density profiles predicted by ESS theory for the unsaturated film situation by comparing them with appropriate Monte Carlo simulations. To our knowledge such simulations have yet to be carried out.

An interesting problem, presently under study, is the behavior of the unsaturated films for very low asymptotic vapor densities. Figure 2 suggests that as  $n_B^0$  is further lowered all filmlike structure will disappear, leaving only a single peak near the substrate. Within the ESS theory this peak can be thought of as a liquid monolayer. Clearly, this monolayer must vanish as  $n_B^0 \rightarrow 0$ . The question arises as to whether or not it vanishes continuously or whether there is discontinuous behavior as might be expected for a "two-dimensional" liquid-vapor transition within the monolayer. Preliminary studies indicate that the latter situation can, indeed, obtain.<sup>17</sup> A thorough study of this effect will form the subject of a future publication.

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### APPENDIX A

Equation (12) is a linear integral equation in one dimension. Before solving it, one needs the kernel  $h_{BB}^0(z'-z)$ ; this was obtained from the PY equation for a uniform Lennard-Jones (6-12) fluid following the procedure described in Ref. 6. Two methods of solution of (12) were employed. The first was

to convert the integral equation into a set of linear inhomogeneous algebraic equations by doing the integration using the extended Simpson's rule for  $-9\sigma \leq z \leq 9\sigma$ . For  $|z| > 9\sigma$ ,  $y(z)$  was assigned its limiting values which are

$$\lim_{z \rightarrow -\infty} y(z) = 1 / \left( 1 + n_B^0 \int_{-\infty}^{\infty} dz' h_{BB}^0(z') \right) \quad (\text{A1})$$

and

$$\lim_{z \rightarrow \infty} y(z) = 1. \quad (\text{A2})$$

The space of  $|z| < 9\sigma$  was divided into 300 intervals of  $0.06\sigma$ , resulting in 301 simultaneous equations which were then solved using Gauss-Jordan elimination.

The second method of solution was by iteration. A guess for  $y(z)$ ,  $y_0(z)$ , was first inserted into the right-hand side of (12), producing a  $y_1(z)$ . Either this function or some linear combination of  $y_0$  and  $y_1$  was reentered on the right-hand side and the procedure repeated until convergence was obtained. A variety of grid sizes ranging down to  $0.025\sigma$  was employed; also, the limits on the range of  $z$  for which  $y(z)$  was found in this way, as opposed to using the limiting values (A1) and (A2), were taken as large as  $|z| = 12\sigma$ .

Comparison of the results obtained by both methods and with different grid spacings shows that the error in the  $n(z)$  reported here is always less than 0.001 and generally less than 0.0001; the error is greatest around the first peak and the following minimum in  $n(z)$  at the higher densities  $n_B^0$ .

## APPENDIX B

The numerical procedure used to find the density profile from the ESS theory is the same as that described in Ref. 7. Basically, a parametrized

trial function is chosen for  $n(z)$  and the free-energy functional is then minimized with respect to variation of the parameters. The trial function used to produce the results at  $T = 1.1$ , shown in Fig. 2, is

$$n(z) = \left( \frac{\beta}{e^{\gamma(z-\delta)} + 1} + \sum_{j=1}^5 \theta_j z^{j-1} e^{-\epsilon z^2} + n_B^0 \right) e^{-\alpha/z^9 T}, \quad (\text{B1})$$

where the variational parameters are  $\alpha, \beta, \gamma, \delta, \epsilon$ , and the five  $\theta_j$ 's. This function can oscillate by virtue of the power series; it varies as  $e^{-\alpha/z^9 T}$  for small  $z$ ; and, for relatively thick films,  $\beta + n_B^0$  is the density of the film,  $\delta$  is its approximate thickness, and  $1/\gamma$  is the width of the transition region between the film and the vapor.

At  $T = 1.4$ , which is above the gas-liquid critical temperature, there is no formation of a filmlike structure having a density significantly larger than  $n_B^0$ . Consequently the term in (B1) which is proportional to  $\beta$  is superfluous in that keeping it does not lead to improved minima of the free-energy functional  $\Omega[n]$ . We have therefore used the trial function

$$n(z) = \left( \sum_{j=1}^5 \theta_j z^{j-1} e^{-\epsilon z^2} + n_B^0 \right) e^{-\alpha/z^9 T} \quad (\text{B2})$$

to arrive at the results reported here. Other trial functions were investigated, but (B2) was judged superior on the basis of minima obtained. Also in all cases, a variety of different starting configurations were employed in order to be sure that the final density profiles are in fact correct. In particular, we tried initial configurations close to those predicted by the LPY theory; they proved to give significantly higher free energies, according to the ESS theory, than those for which  $\Omega[n]$  is actually minimized.

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<sup>10</sup>E. Helfand, H. L. Frisch, and J. L. Lebowitz, *J. Chem. Phys.* **34**, 1037 (1961).

<sup>11</sup>See Eq. (11).

<sup>12</sup>H. C. Anderson, J. D. Weeks, and D. Chandler, *Phys. Rev. A* **4**, 1597 (1971).

<sup>13</sup>As seen from the above discussion, this designation is not really precise for the work of Ref. 5.

<sup>14</sup>The potential parameters are such that the hard-core diameter is the mean of the CO<sub>2</sub> and argon hard-core diameters while the Van der Waals attraction is equal to the square root of the product of the argon and CO<sub>2</sub> Van der Waals attractions. The argon interaction was chosen as in Ref. 6 while the CO<sub>2</sub> potential was taken from J. A. Hirschfelder, C. F. Curtiss, and R. B. Bird [*Molecular Theory of Gases and Liquids* (Wiley, New York, 1954), p. 1111]. Finally,  $n_w$  is the number density of solid CO<sub>2</sub> at  $T = 100$  K as reported by O. Maass and W. H. Barnes [*Proc. R. Soc. A* **111**, 224 (1926)].

<sup>15</sup>These results are taken from a Letter, Ref. 7, whose focus is rather different from that of the present work.

<sup>16</sup>This trend continues for larger  $n_B^0$ , but for larger  $n_B^0$ , there are some uncertainties in the ESS theory due to large first-peak densities.

<sup>17</sup>Such behavior has been found for a simple sticky-hard-sphere-sticky-hard-surface model in the Percus-

Yevick approximation by J. W. Perram and E. R. Smith [Phys. Lett. 59A, 11 (1976)]. An excellent review of the subject, dealing with both experiment and theory, is found in J. G. Dash, *Films on Solid Surfaces* (Academic, New York, 1975).