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Nonadditive hard discs, a model for partially localized adsorption

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It is shown how one can approximate partially localized adsorbed layers of molecules on surfaces by a mixture of hard discs with negatively nonadditive diameters. The thermodynamic properties for this reference state are found with a particular version of scaled particle theory. The contribution of the attractive forces is obtained from a perturbation expansion where we keep the two leading terms. The radial-distribution function of the reference state for this contribution is obtained from a virial expansion. The calculations are carried out for a square-well potential. We calculate numerically the following results: The degree of localization, i.e., the concentration of particles in the localized state, the equation of state, i.e., spreading pressure as a function of coverage, the isotherms, and the isosteric heat of adsorption. These quantities are calculated for different values of the adsorbate-adsorbent lattice mismatch, the height of the barrier to lateral diffusion on the surface, the strength of the attractive forces, and the temperature and pressure. The attractive forces favor out-of-registry adsorption against localized adsorption. The localization effects lead to a noticeable decrease in the critical temperature for two-dimensional condensation even in highly mobile adsorbed layers.

I. INTRODUCTION

When molecules adsorb on the surface of a solid, there are two, relatively easy to treat, limiting situations:

(i) If the difference between the free enthalpy of adsorption on different sites of the solid is much smaller than the thermal energy kT, and if the minimum of the gas-solid potential is at the same distance at every site, the molecules will be free to arrange themselves into an average configuration which corresponds to a two-dimensional fluid or solid. One speaks of mobile adsorption.

(ii) If the energy barrier that separates two identical sites is much larger than the thermal energy, molecules will be frozen into their sites, and if the smallest distance between sites is larger than the molecular diameter we will have localized adsorption.

While the two limiting cases have always met considerable attention, there are only very few attempts to solve the intermediate problem of partially localized adsorption, when one cannot neglect the influence of the substrate on the adsorbed mobile layer.[1] The basic equations for this problem were laid down by Hill and Steele[2-4] in the early sixties.

One of the reasons for the timid advance was certainly the lack of data on the variation of adsorption energies along the surface or even the exact value. In the meantime much more information is available from scattering experiments[5] followed by exact scattering calculation[6] or detailed calculations of the adsorption energy either by lattice summation[7] or by direct solution of the Schrödinger equation.[8]

At the same time, the diffraction data, e.g., from low-energy electron diffraction (LEED)[9] and from other techniques,[10] on adsorption have revealed a large amount of detail, such as transitions between different configurations. Globally the situation can be represented by a temperature-coverage diagram. The first complete diagram of this kind was established for CO adsorption on palladium.[11] Of course not all the diagram is always measurable since it describes the idealized case of monolayer adsorption. From a certain coverage on, adsorption of the next layer will set in, ending the compression of the first layer.

The interest in the growth mode of a layer on a solid is not merely academic. Indeed the structure of the first monolayer of e.g., a solid grown onto another will condition the properties of the whole deposit in physical vapor deposition (PVD). Out-of-registry epitaxy will lead to perfect growth conditions for the nascent solid, while with in-registry adsorption the interface will be a source of defects, mechanical weakness, etc. The global nature of the statistical mechanical approach has the following advantages over microscopic theories of a solid-gas couple: One can treat a large class of experiments, since partially localized adsorption will occur:

(a) for noble-gas adsorption onto inert solids like graphite and the transition-metal dichalcogenides at very low temperatures in ultrahigh vacuum.

(b) for reactive gases like hydrogen and oxygen on the transition metals for high temperatures in ultrahigh vacuum or in the presence of a background of inert gases.

(c) in so-called contact adsorption of solutes from solutions, since the results do not change qualitatively if one replaces the vacuum by a solvent.

Therefore we chose for this paper an approach that is not conditioned by a particluar gas-solid pair, but describes all results by a few parameters which, when identified with particular constants, should allow the understanding of the properties of a particular adsorbate-adsorbent system.

II. TWO-DIMENSIONAL APPROXIMATION

The general situation of adsorbed molecules on a solid is complex. In principle neither the free adsorption enthalpy nor the minimum of the gas-solid interaction potential will be independent of the site. As a matter of fact, these two quantities must not even coincide in chemisorption where, e.g., the different site configurations correspond to different valencies.

A sitewise separation of the motion parallel to the surface from the motion normal to the surface represents a good approximation for many systems. Indeed if one represents the motion for small amplitudes by a harmonic oscillator, one has for most cases,[12]

$$\omega_\perp \gg \omega_\parallel ,$$

$\perp$, $\parallel$ with respect to the geometric surface. The adsorbate molecules, while partially mobile on the surface will be frozen into the lowest vibrational state of adsorption. If the geometric surface does not coincide with the locus of the minimum of energy, the separation of the motion into normal and parallel components, requires furthermore, that the activation energy for the diffusion on the surface be smaller than the energy difference between the ground state and the first excited state of the vibration normal to the surface.

$$\Delta G_{\text{ads}} < \hbar(\omega_\perp^0 - \omega_\perp^1) . \tag{1}$$

A considerably better way to a two-dimensional approximation would consist in the use of the surface of the minimum of the adsorption energy as a plane on which the adsorbate is located. However, the corresponding coordinate transformation "forbids" any further treatment by statistical-mechanical means, since the distances between molecules relevant for the interaction will no longer coincide with the distance on this surface.

To put these arguments in a more formal manner, consider the partition function of M particles at positions $(\vec{R}_1 \ldots \vec{R}_M)$, in a volume V, and at a temperature $T = 1/\beta k$, in contact with an adsorbent wall.

$$Z_M = \int d\vec{R}_1 \cdots d\vec{R}_M \exp[-\beta(U_M^2 + U_M^1)] . \tag{2}$$

We have separted the interactions into the interparticle potential

$$U_M^2 = \sum_{i,j}^{M} U_{ij}(\vec{R}_{ij}) , \tag{3}$$

and the particle-wall interaction

$$U_M^1 = \sum_{i=1}^{M} U_i(\vec{R}_i) , \tag{4}$$

but neglected the many molecule interactions. U_{ij} may be an effective, renormalized pair potential which includes the effect of the substrate on the interaction between two adsorbed particles. We split the coordinate $\vec{R}_i$ into a component normal to the surface z_i, and a component parallel to the surface, $\vec{r}_i$

$$\vec{R}_i = \vec{r}_i + z_i \vec{n} . \tag{5}$$

Then our first assumption reads

$$U_{ij}(\vec{R}_i, \vec{R}_j) = \begin{cases} U_{ij}(r_{ij}) , & 0 \leq z_i \leq z_n \quad (6) \\ \text{and } 0 \leq z_j \leq z_n , & \\ 0 , & z_i > z_n \text{ or } z_j > z_n . \quad (7) \end{cases}$$

The second equation is just a convenient way to introduce the usual assumption, that the bulk gas is ideal. Our second assumption is the separability of the one-particle potential.

$$U_i(\vec{R}_i) = U_i(z_i) + \Delta U_i(\vec{r}_i) . \tag{8}$$

Under these conditions we can use two-dimensional (2-D) partition functions[3a]

$$Z_N^{(2D)} = \int \cdots \int d^2 r_1 \cdots d^2 r_N \, p_0^{\{N\}}(\vec{r}^N) \times \exp[-\beta U_N^2(\vec{r}^N)] , \tag{9}$$

where N is the number of molecules adsorbed, and

$$p_0^{\{N\}}(\vec{r}^N) = \frac{\exp\left(-\beta \sum_{i=1}^{N} \Delta U_i(\vec{r}_i)\right)}{\left(\int d\vec{r}_i e^{-\beta \Delta U_I(\vec{r}_i)}\right)^N} . \tag{10}$$

This partition function can be used to calculate the chemical potential of the adsorbate particles in the usual way:

$$\beta(\mu - {}^0\mu) = -(\partial \ln Z_N^{(2D)} / \partial N)_{T,A} . \tag{11}$$

${}^0\mu$ refers to the ideal two-dimensional adsorbate.

$$\beta^0\mu = \ln\zeta N\lambda^2 - \frac{\partial}{\partial N}(\ln Z_1^{(s)})^N = \ln\left(\frac{\zeta N\lambda^2}{Z_1^{(s)}}\right), \tag{12}$$

with

$$Z_1^{(s)} = \int d\vec{\mathrm{R}}_i(e^{-\beta U_i(\vec{\mathrm{R}}_i)} - 1), \tag{13}$$

ζ and λ, the momentum partition function for the motion perpendicular viz. parallel to the surface. Steele has shown that the canonical partition function of the adsorbed gas Z_N^s is related to the (2-D) canonical partition function $Z_N^{(2\mathrm{D})}$ through[3b]

$$Z_N^{(s)}/(Z_1^{(s)})^N = Z_N^{(2\mathrm{D})}. \tag{14}$$

The equation of state is then found in the usual way as

$$\beta\Phi = \left(\frac{\partial \ln Z_N^{(s)}}{\partial A}\right)_{T,N} = \left(\frac{\partial \ln Z_N^{(2\mathrm{D})}}{\partial A}\right)_{T,N}, \tag{15}$$

where Φ is the spreading pressure and A, the surface area. We also define the coverage Θ:

$$\Theta = N/A. \tag{16}$$

III. SEPARATION OF THE POTENTIAL

We intend to use a perturbation scheme to calculate the equation of state. To this end we split the potential into two parts:

$$U_{ij}(\vec{\mathrm{r}}) = U_{ij}^0(r) + \tilde{U}_{ij}(\vec{\mathrm{r}}), \tag{17}$$

$$U_{ij}^0(r) = \begin{cases} \infty\, |\vec{\mathrm{r}}| \leqslant a \\ 0\, |\vec{\mathrm{r}}| > a, \end{cases} \tag{18}$$

$$\tilde{U}_{ij}(\vec{\mathrm{r}}) = U_{ij}(\vec{\mathrm{r}}) \quad |\vec{\mathrm{r}}| > a. \tag{19}$$

a can in principle be obtained from the repulsive part of an analytical intermolecular potential.[15] For example, in the case of an exponential repulsive potential

$$U_{ij}(r) = Ae^{-r/r_0},$$

we would have[18]

$$a = r_0(\ln A/kT + C), \tag{20}$$

where C = Euler's constant.

We introduce the separation of the potential into Eq. (9) and make a Taylor expansion of the logarithm of the partition function towards the strength of the attractive potential which we scale by a parameter ρ.

$$\ln Z_N^{(2\mathrm{D})}(\rho) = \ln \int\cdots\int d^2r_1\cdots d^2r_N p_0^{\{N\}}(\vec{\mathrm{r}}^N) \times e^{-\beta U_N^0(\vec{\mathrm{r}}^N)}e^{-\beta\rho\tilde{U}_N(\vec{\mathrm{r}}^N)}, \tag{21}$$

$$\ln Z_N^{(2\mathrm{D})}(\rho) = \ln Z_N^{(2\mathrm{D})}(\rho=0) + \rho\left(\frac{\partial}{\partial\rho}Z_N^{(2\mathrm{D})}\right)_{\rho=0} + \cdots. \tag{22}$$

The mixture with $\rho = 0$ is our reference state. We shall distinguish variables referring to it by a right upper 0.

$$\ln Z_N^{(2\mathrm{D})}(\rho) = \ln Z_N^{0(2\mathrm{D})} - \beta\rho\,\frac{\int\cdots\int d^2r_1\cdots d^2r_N p_0^{\{N\}}(\vec{\mathrm{r}}^N)\sum_{kl}\tilde{U}(\vec{\mathrm{r}}_k - \vec{\mathrm{r}}_l)e^{-\beta U_N^0(\vec{\mathrm{r}}^N)}}{\int\cdots\int d^2r_1\cdots d^2r_N p_0^{\{N\}}(\vec{\mathrm{r}}^N)e^{-\beta U_N^0(\vec{\mathrm{r}}^N)}}$$

$$= \ln Z_N^{0(2\mathrm{D})} - \frac{\beta\rho}{Z_N^{0(2\mathrm{D})}}\frac{N(N-1)}{2}\int d^2r_1\,d^2r_2\tilde{U}(\vec{\mathrm{r}}_1 - \vec{\mathrm{r}}_2)\int d^2r_3\cdots d^2r_N\, p_0^{\{N\}}(\vec{\mathrm{r}}^N)e^{-\beta U_N^0(\vec{\mathrm{r}}^N)}. \tag{23}$$

Neglecting the difference between N and $N-1$ and comparing the last expression with the definition of the radial distribution function for the reference state,

$$g^0(\vec{\mathrm{r}}_1, \vec{\mathrm{r}}_2) = A^2\,\frac{\int\cdots\int d^2r_3\cdots d^2r_N\, p_0^{\{N\}}(\mathrm{r}^N)e^{-\beta U_N^0(\vec{\mathrm{r}}^N)}}{\int\cdots\int d^2r_1\cdots d^2r_N\, p_0^{\{N\}}(\mathrm{r}^N)e^{-\beta U_N^0(\vec{\mathrm{r}}^N)}}, \tag{24}$$

one sees that for an isotropic mixture the first two terms of the perturbation expansion can be written as

$$\ln Z_N^{0(2\mathrm{D})} = \ln Z_N^{0(2\mathrm{D})} - \frac{\beta N^2}{2A}\int d^2r\,\tilde{U}(\vec{\mathrm{r}})g^0(\vec{\mathrm{r}}). \tag{25}$$

It can be shown that an expansion in terms of Ursell-Mayer functions leads to the same result.

IV. THE REFERENCE SYSTEM

The reference system is a mixture of particles interacting with a hard-sphere potential. Each of the particles interacts with the adsorbent via its adsorption potential $U_i(\vec{\mathrm{r}})$. A very useful model of this reference system is a binary mixture of nonadditive hard discs, which was first proposed by Holland.[13] One arrives at it in the following way:

The hard-sphere diameter a_{mm} describes fully the interaction between two mobile particles. Two localized particles exclude each other from adsorption sites, whose distance we call a_{ll}. To represent the fluid of localized particles as a hard sphere fluid may at first appear a very crude approximation, since the particles constitute a lattice and are not free to pack around a central localized particle in an arbitrary form. But since most fluid theories make significant approximations for the second shell anyhow, the model is reasonable in this framework. We do of course not expect to obtain a reasonable description of the localized solid. However, this approximation allows one to avoid Steele's two-parameter expansion.[3(a)]

A localized particle interacts with a mobile particle with the same diameter as two mobile particles, a_{mm}. Therefore, in the notation of hard-disc mixtures

$$a_{ml} = a_{mm} = \tfrac{1}{2}(a_{mm} + a_{ll}) - \tfrac{1}{2}(a_{ll} - a_{mm}) . \tag{26}$$

Once the diameters, the temperature and total coverage are specified, we must determine $X_{l,m} = \Theta_{l,m}/\Theta$ and the equation of state. For this we have the additional condition of "chemical equilibrium" between mobile and localized absorbed particles.

$$\mu_l^0 = \mu_m^0 . \tag{27}$$

The chemical potentials are obtained by adding the work functions, which we will obtain from our fluid theory to the two *different* ideal chemical potentials. This difference arises from the difference in $Z_1^{(s)}$ in Eq. (13).

We shall use scaled particle theory for the description of the reference state.[14] We have shown already that this theory gives currently the best results for mixtures of negatively nonadditive hard spheres.[14(b)] We will repeat here only the essential results and those modifications which are necessary for this particular problem.

The concept of scaled particle theory is simple. One replaces the intermolecular potentials of one particle of each species by a scaled interaction,

$$U_{ij}(r) \to U_{ij}[r/\xi_{ij}(\lambda)] \quad i, j = l, m . \tag{28}$$

This particle will then be called a localized (mobile) cavity of size λ. Next we consider the work, which is necessary for the insertion of such cavities, $W_{l,m}(\lambda)$. One can show, that this work is known exactly up to a certain size $\bar{\lambda}_{l,m}$

$$W_i(\lambda) = -kT \ln\left\{1 - \pi \sum_{j=l,m} \Theta_j [a_{ij}\xi_{ij}(\lambda)]^2\right\}, \quad i = l, m . \tag{29}$$

For larger values of λ, we approximate it by a Taylor expansion

$$W_i(\lambda) = \sum_{k=0}^{2} W_i^k (\lambda - \bar{\lambda}_i)^k , \quad i = l, m . \tag{30}$$

The first two coefficients of this expansion are best obtained from the continuity of $W_{l,m}(\lambda)$ and its first derivative at $\bar{\lambda}_{l,m}$. Since we want to avoid repeating the derivation of scaled particle theory for nonadditive hard spheres we will use our previous notation for binary mixtures[14]:

$$a_{mm} = a , \quad a_{ll} = a(1+\nu) , \quad (\Delta = -\tfrac{1}{2}\nu) . \tag{31}$$

We show in Appendix A why in the present case the scale function

$$\xi_{ij}(\lambda) = \lambda , \quad i, j = l, m , \tag{32}$$

is the only consistent choice for a binary mixture with $\Delta = -\frac{1}{2}\nu$. The spreading pressure ϕ is related to the different work functions through the virial relation

$$\frac{\beta\phi^0}{\Theta} = 1 + \tfrac{1}{4}\beta \sum_{i=l,m} x_i \left(\frac{\partial W_i(\lambda)}{\partial\lambda}\right)_{\lambda=1} . \tag{33}$$

We skip over the calculation which leads to the following results for the coefficients and $\bar{\lambda}_i$'s:

$$\bar{\lambda}_m = \tfrac{1}{2} , \ \bar{\lambda}_l = \frac{1}{2+\nu} , \tag{34}$$

$$W_m^0 = -kT \ln(1-\theta) , \tag{35}$$

$$W_l^0 = -kT \ln\{1 - (1+\tfrac{1}{2}\nu)^{-2}\theta[x_m + (1+\nu)^2 x_l]\} , \tag{36}$$

$$W_m^1 = kT 4\theta/(1-\theta) , \tag{37}$$

$$W_l^1 = \frac{4\theta[x_m + x_l(1+\nu)^2](1+\nu/2)^{-1}}{1 - (1+\nu/2)^{-2}\theta[x_m + x_l(1+\nu)^2]} , \tag{38}$$

where $\theta = a_0\Theta$ with $a_0 = \frac{1}{4}\pi a^2$.

To determine $W_{m,l}^2$ we must consider the limit of very large λ, where the cavity can be considered as macroscopic. Simple hard spheres lead to spherical cavities in the fluid from which all particles are excluded. In our case this is only true for mobile cavities. With nonadditive interactions, the cavity from which all particles are excluded will be surrounded by a shell whose outer envelope is a semipermeable membrane. For a binary mixture the shell contains a pure fluid of the opposite (same) species for negative (positive) nonadditivity (see Fig. 1). An osmotic pressure develops across the membrane. The coverage of the pure fluid inside differs from both total and partial coverage in the bulk fluid, since it is

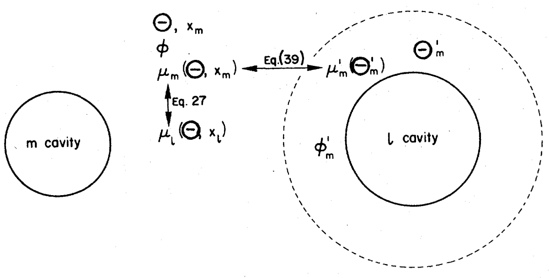

FIG. 1. Macroscopic limit of the scaled particle theory. It shows the difference between the localized and mobile cavity for this particular nonadditivity. Also included are the numbers of the equations that connect the various quantities.

determined by the condition of the constancy of its chemical potential across the membrane. If we distinguish the quantities in the shell of the localized cavity by a prime, this condition reads

$$\mu_m^0(\Theta, x_m) = \mu_m'^0(\Theta_m') . \tag{39}$$

$W^2_{m,l}$ is proportional to the work necessary to insert these macroscopic cavities into the fluid, which is simply the product of the corresponding spreading pressures and enclosed volumes

$$W_m^2 = \pi a^2 \phi^0 , \tag{40}$$

$$W_l^2 = \pi a^2 \{(1+\nu)^2 \phi^0 + [1-(1+\nu)^2]\phi_m'^0\} . \tag{41}$$

For the relations between $\phi_m'^0$, $\mu_m'^0$, and θ_m' we use the results from the scaled particle theory of pure hard-disc fluids[16]

$$a_0 \beta \phi_m'^0 = (1-\theta_m')^{-2}\theta_m' , \tag{42}$$

$$\beta\mu_m'^0 = \beta\,{}^0\mu_m + \ln\frac{\theta_m'}{(1-\theta_m')} + \frac{\theta_m'(3-2\theta_m')}{(1-\theta_m')^2} , \tag{43}$$

so that we finally arrive at three coupled transcendental equations for ϕ^0, θ_m', and x_m:

(i) The membrane equation, [Eq. (39)]:

$$\frac{\beta\pi}{4} a^2 \phi^0 = \ln\frac{\theta_m'^2(1-\theta)}{x_m\theta(1-\theta_m')} - \frac{2\theta}{1-\theta} + \frac{\theta_m'(3-2\theta_m')}{(1-\theta_m')^2} . \tag{44}$$

(ii) The virial relation, Eq. (33):

$$\begin{aligned}\frac{\beta a_0 \phi^0}{\theta} = Z = &\left(1 - x_m\theta - 2(1-x_m)\theta\,\frac{(1+\nu)^3}{2+\nu}\right)^{-1}\\ &\times\left(1 + x_m\frac{\theta}{1-\theta} + (1-x_m)(2+\nu)^2\,\frac{(1+\nu)^2 - x_m\nu(2+\nu)}{(2+\nu)^2 - 4\theta[(1+\nu)^2 - x_m^2(2+\nu)]}\right.\\ &\left.\quad - 2\,\frac{1+\nu}{2+\nu}\,\pi a^2(1-x_m)\nu(2+\nu)\,\frac{\theta_m'}{(1-\theta_m')^2}\right) .\end{aligned} \tag{45}$$

(iii) The condition of chemical equilibrium, Eq. (27):

$$\begin{aligned}\beta({}^0\mu_m - {}^0\mu_l) + \ln\frac{x_m}{1-x_m} = &\ln\left\{1 - 4\theta\left[\left(\frac{1+\nu}{2+\nu}\right)^2 - x_m\frac{\nu}{2+\nu}\right]\right\} - \ln(1-\theta)\\ &+ \frac{4\theta(2+\nu)(1+\nu)[(1+\nu)^2 - x_m\nu(2+\nu)]}{(2+\nu)^2 - 4\theta[(1+\nu)^2 - x_m\nu(2+\nu)]} - \frac{2\theta}{1-\theta} + \pi a^2\phi^0\,\frac{\nu(4+3\nu)}{4(2+\nu)^2}\\ &- 4\,\frac{\nu(1+\nu)^2}{2+\nu}\,\frac{\theta_m'}{(1-\theta_m')^2} .\end{aligned} \tag{46}$$

These three equations can be used to calculate numerically the equation of state for the reference system. The barrier towards lateral translation is given by the difference of the ideal chemical potentials of the two adsorbates

$${}^0\mu_m - {}^0\mu_l = \epsilon_m - \epsilon_e = \Delta\epsilon .$$

In Fig. 2 we have made the usual plot of the compressibility factor z as a function of the reduced mixture coverage

$$\theta^* = \pi/16a^2[3 + (1+\nu)^2]N/A .$$

One sees in this representation, which includes the nonadditivity in the abscissas, that a "law of corresponding states" prevails between different mixtures. But for very high nonadditivity one can observe a phase transition at high coverage which leads to an ordered state. Therefore the curve for $\nu = 0.9$ terminates at $\theta^* = 0.55$. At this coverage Z drops in fact sharply in the same way as observed previously[14(c)] for symmetrical mixtures ($\nu = 0$, $\Delta < 0$). But in this case the representation of Fig. 3, where we give the excess compressibility as a function of composition for different coverages is more revealing. It shows how the minimum of the excess moves to higher concentrations of the localized discs as the reduced coverage increases.

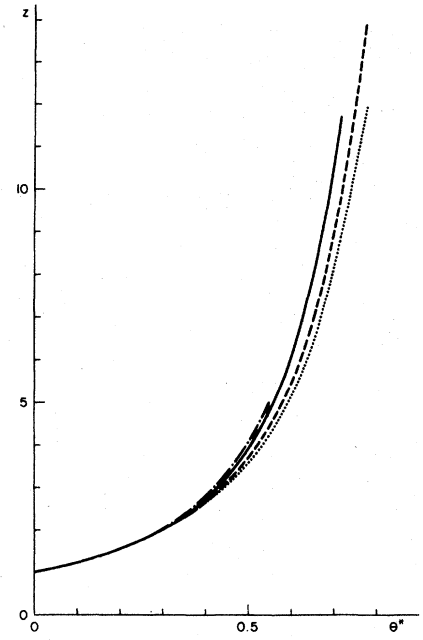

FIG. 2. Compressibility factor as a function of reduced coverage for nonadditive hard-disc mixtures of on the equicomposition line, for different nonadditivities: —·—: $\nu=0.9$, ... $\nu=0.5$, -----: $\nu=0.2$, —— $\nu=0.05$.

In general Z_{ex} attains its minimum value when on the average the maximum number of dislike particles are in contact with one another. This means that the concentration X_m^*, at the minimum of $Z_{ex}-X_m^*=\theta_m^*/\theta$, is the point at which the coordination of l particles (the solvent) around m particles (the solute) is largest for a given θ, or where the largest amount of clusters of l particles with an m particle at the core exists. Considering Fig. 4, then, we see that at relatively low densities ($\theta=0.3$) the proportion of m to l particles is 1 to 2 at the minimum ($X_m^*=0.35$). Thus for $\theta=0.3$ three particle clusters l-m-l are the most abundant at the minimum of the compressibility. For $\theta=0.4$ $X_m^*\approx 0.25$, and the majority of clusters are $3l$ particles enveloping one m particle At $\theta=0.5$ Z_{ex} falls off rather abruptly at the minimum and the coordination number of the l particles around an m core particle is 9. The reverse situation of large m clusters with l particles in their core does not lead to as large a drop in Z_{ex}.

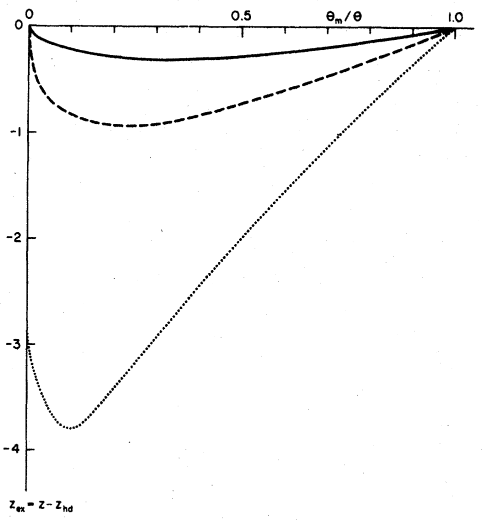

FIG. 3. Nonadditivity, excess of the compressibility factor of negatively nonadditive hard discs as a function of composition for different coverages: ——: $\theta=0.3$, ----- $\theta=0.4$, ... $\theta=0.5$.

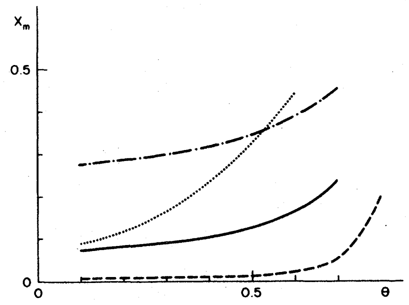

FIG. 4. "Composition," X_m, of the adsorbed reference system as a function of coverage θ for different values of nonadditivity and height of the barrier to surface migration: $\nu=0.05$: ----- $\Delta\epsilon/T=5$, ——— $\Delta\epsilon/T=2.5$ $\nu=0.2$: ..... $\Delta\epsilon/T=2.5$.

V. THE PERTURBATION EXPANSION

We continue the development from Eq. (25). We still have to take into account that we use a mixture as model for our reference system. In this case Eq. (25) reads

$$\ln Z_N^{(2D)}=\ln Z_N^{0(2D)}-\frac{N_m^2}{2A}\beta\int d^2r\,\tilde{U}(r)g_{mm}^0(r)$$
$$-\beta\frac{N_mN}{A}\int d^2r\,\tilde{U}(r)g_{ml}^0(r)$$
$$-\beta\frac{N_l^2}{2A}\int d^2r\,\tilde{U}(r)g_{ll}^0(r)\,, \tag{47}$$

where we have of course taken the same attractive force for mobile and localized particles. The corresponding perturbation expansions for the chemical potentials and the spreading pressure follows from the gradients towards the partial numbers and the surface area

$$\mu_m=\mu_m^0+\frac{1}{2A}\int d^2r\,\bar U(r)\,\frac{\partial}{\partial N_m}[N_m^2 g_{mm}^0(r)]$$
$$+\frac{N_l}{A}\int d^2r\,\bar U(r)\,\frac{\partial}{\partial N_m}[N_m g_{ml}^0(r)]\,. \tag{48}$$

$$\mu_l=\mu_l^0+\Theta x_m\int d^2r\,\bar U(r)\,\frac{\partial}{\partial N_l}[N_l\, g_{ml}^0(r)]$$
$$+\frac{1}{2A}\int d^2r\,\bar U(r)\,\frac{\partial}{\partial N_l}[N_l^2 g_{ll}^0(r)]\,. \tag{49}$$

$$\phi=\phi^0-N_m^2\tfrac{1}{2}\int d^2r\,\bar U(r)\,\frac{\partial}{\partial A}[A^{-1}g_{mm}^0(r)]$$
$$+N_mN_l\int d^2r\,\bar U(r)\,\frac{\partial}{\partial A}[A^{-1}g_{ml}^0(r)]$$
$$-\tfrac{1}{2}N_l^2\int d^2r\,\bar U(r)\,\frac{\partial}{\partial A}[A^{-1}g_{ll}^0(r)]\,. \tag{50}$$

A. Radial distribution functions of the reference state

Having opted for scaled particle theory for the equation of state of the reference system, we need another way to find a decent approximation for the radial distribution functions. But since we shall use it only to calculate the linear terms of our perturbation expansion, the first two terms of the virial expansion are a consistent choice after all. Representing them diagrammatically, we have for our mixture

$$g_{ij}^0(r)=\exp[-\beta U_{ij}(r)]\Big(1+\sum_k \underset{i\quad j}{\overset{k}{\wedge}}+\cdots\Big)$$
$$=g_{ij}^{01}(r)+\Theta g_{ij}^{02}(r)\,, \tag{51}$$

or writing out the different terms explicitly for first and second order, respectively

$$g_{ij}^{01}(r)=\begin{cases}0\,, & r<a_{ij}\\ 1\,, & r>a_{ij}\end{cases} \tag{52}$$

$$\theta g_{ij}^{02}(r)=\sum_k \theta_k\, g_{ij,k}^0\,. \tag{53}$$

In this notation the comma separates the index of the species over whose position one must integrate. In our special case then

$$g_{mm}^{02}(r)=\begin{cases}0\,, & r>2a\\ g_{mm,m}(r)\,, & 0<r<2a\end{cases} \tag{54}$$

$$g_{ml}^{02}=\begin{cases}0\,, & r>a(2+\nu),\\ \theta_m/\theta g_{ml,m}(r)+\theta_l/\theta g_{ml,l}(r)=\theta_m/\theta g_{mm,m}(r)+\theta_l/\theta g_{ml,l}(r)\,, & \nu a<r<a(2+\nu)\end{cases} \tag{55}$$

$$g_{ll}^{02}=\begin{cases}0\,, & r>2a(1+\nu)\\ \theta_m/\theta g_{ll,m}(r)+\theta_l/\theta g_{ll,l}(r)\,, & 0<r<2a(1+\nu)\,.\end{cases} \tag{56}$$

The explicit expressions for these terms are given in Appendix C. It is also important that $g_{ml,l}^{02}(r)$ is the only nonsymmetric integral.

B. Square-well potential

We will calculate the perturbation terms for the simplest case of a square-well potential. This we hope will later allow comparison with the effort of exact computer simulations on square-well fluids. In this case we have

$$\bar U(r)=\begin{cases}-\epsilon\,, & a\leqslant r\leqslant \chi a\\ 0\,, & \chi a<r\end{cases} \tag{57}$$

Furthermore we will restrict the calculation to $\chi>(1+\nu)$, in this case

$$-\int_{a_{ii}^2}^{\infty} dr\,r\bar U(r)=\tfrac{1}{2}\epsilon[(\chi a)^2-a_{ii}^2]\,. \tag{58}$$

Many integrals differ only by their integration limits, which for the following we shall summarize as δ for the upper and σ for the lower limit. This leaves us with two types of integrals $J_{ii,jj}(\delta,\sigma)$ and $J_{ii,ii}(\delta,\sigma)$ which are given explicitly in Appendix C.

VI. ADSORBATE EQUATION OF STATE, THE ISOSTERIC HEAT AND THE ADSORPTION ISOTHERM

Having found the perturbation terms, we can calculate an equation of state that combines the results for the reference system Eqs. (44)–(46) with the results from perturbation theory Eqs. (C7)–(C11). Numerical solutions of these equations can be obtained in a straightforward manner.

A more interesting quantity to look for is the isosteric heat of adsorption, since it has a cusp at any possible phase transition of the fluid. It is defined as

$$q=kT^2\left(\frac{\partial\,\ln p}{\partial T}\right)_\theta\,. \tag{59}$$

As a function of coverage q displays a decreasing sigmoid like behavior at low temperatures but a monotonic decrease at high temperatures (compare with Ref. 13). We calculate the isotherm from

$$\mu_m = \mu_l = \mu'_m = \mu_G\,, \tag{60}$$

where μ_G is the chemical potential of the bulk gas, which we will consider ideal

$$\beta\mu_G = \ln\Lambda^3/kT + \ln p = \beta\mu_G^0 + \ln p\,. \tag{61}$$

We sum up the adsorbate chemical potentials as

$$\begin{aligned} \beta\mu_m &= \beta\mu_m^* + \ln\theta_m + \beta\mu_m^\epsilon = \beta^0\mu_m + \beta\mu_m^\epsilon\,, \\ \beta\mu_l &= \beta\mu_l^* + \ln\theta_l + \beta\mu_l^\epsilon\,, \end{aligned} \tag{62}$$

where the μ^*'s are defined through Eqs. (12) and (62); where the excess chemical potentials are defined by a comparison of Eq. (62) with Eqs. (C10), (48), and (49). Then we can write the isotherm as

$$p = \exp(\beta\mu_m^* - \beta\mu_G^0)\theta_m \exp(\beta\mu_m^\epsilon)\,,$$

or, (63)

$$p^* = p\exp(\beta\mu_G^0 - \beta\mu_m^*) = \theta_m \exp(\beta\mu_m^\epsilon)\,.$$

Similarly, by differentiation

$$q^* = kT^2 \frac{\partial}{\partial T}(\ln\theta_m + \beta\mu_m^\epsilon)_\theta = \text{const}\,. \tag{64}$$

Note that though θ is kept constant in this derivation, θ is temperature dependent through the variation of the mobile-to-localized ratio with temperature. The explicit expressions for the thermodynamic properties are given in Appendix D.

VII. DISCUSSION

In discussing the phenomena of partially localized adsorption the following parameters should be considered: a_{ll}—the characteristic dimension of the adsorption site which may be, e.g., the Wigner-Seitz cell diameter of the two-dimensional lattice of adsorbent atoms. a_{mm}—the collision diameter between two adsorbed particles at a given temperature (note that we have used a temperature-independent collision diameter in this work, which is not always accurate). ϵ_l—the adsorption energy of the localized particles. $\Delta\epsilon$—the height of the barrier to lateral translation of the adsorbed particles.

The attractive force is first characterized by the parameter ϵ—the minimum in the attractive pair potential. For our calculations we used as attractive force a square-well potential of a range χa [see Eq. (57)].

Since a systematic evaluation of the effect of all these parameters and their mutual effects is a paramount task we will limit our discussion to some qualitative, but rather fundamental phenomena. We hope that our general equations can be used for specific applications whenever these parameters are known. We start with a discussion of the adsorption of the reference system. In Fig. 4, where we plot the composition as a function of coverage, one distinguishes two extreme cases:

(i) With large barriers to lateral translation or at low temperatures, the localized particles are favored over the mobile ones up to high coverages, where a relatively abrupt transition to a mobile fluid takes place. This is accompanied by a sharp increase of the necessary pressure of the bulk gas, as can be seen from the isotherm, Fig. 5. This adsorption isotherm resembles the result of the calculations for lattice gases, the Langmuir isotherm very closely. This is remarkable insofar, as we have used a pure fluid model for these localized particles.

(ii) With small barriers, the transition from localized to mobile is gradual. The same gradual behavior is observed in the isotherm.

These differences become still clearer in the plot of the isosteric heat, Fig. 6. Systems with a high $\Delta\epsilon/T$ ratio exhibit an almost density-independent isosteric heat up to high densities, followed by a steep decrease due to the "melting" of the localized particles into mobile ones. On the contrary systems having low $\Delta\epsilon/T$ ratios "melt" gradually, and thus the isosteric heat falls off gradually.

We now turn to the solution of the complete system with the attractive forces. We have chosen results from above and below the critical temperature of two-dimensional condensation. We start with the dependence of the composition on the coverage, Fig. 7.

Generally, compared with the reference system, the inclusion of attractive forces leads to a higher concentration of the mobile particles, having the same ν and the ratio $\Delta\epsilon/T$. This is easily understood since a localized particle can be approached closer by a mobile particle than by another localized particle. The effect would be even more

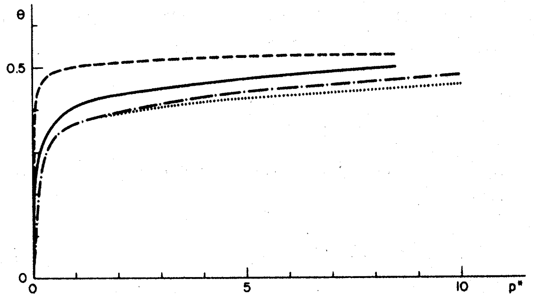

FIG. 5. Adsorption isotherm for the reference system, coverage θ as a function of reduced pressure, p^* for different combination of nonadditivity and barrier height: same parameters as Fig. 4.

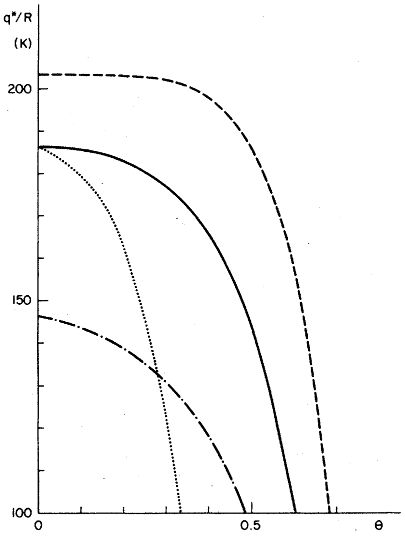

FIG. 6. Isosteric heat of adsorption, q^*, for the reference system as a function of coverage θ. Same parameters as Fig. 6.

pronounced, had we chosen an inverse power law for the attractive part of the potential instead of the square-well form. We see further from Fig. 7 that below the (2-D) critical point the localized particles abound in the (2-D) gas (low-density phase), but the mobile particles largely exceed the localized ones in the liquid phase. On the other hand above T_c(2-D) the composition curve resembles the one found previously for the reference system.

Comparing now the spreading pressure and the adsorption isotherms, Figs. 8 and 9 with their results of the reference system, Figs. 2 and 5, we note the following points:

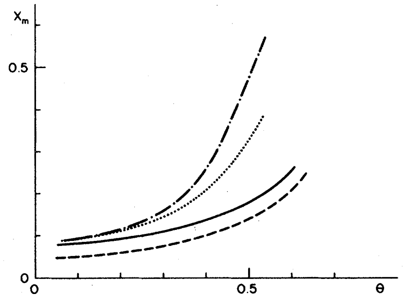

FIG. 7. Localization, $=1-X_m$, in the adsorbate as a function of coverage for different values of nonadditivity and temperature with barrier height $\Delta\epsilon/k=200$ K, square-well depth $\epsilon/k=69.4$ K square-well width $\chi=1.85$ and $T=120$ K: -•-•- $\nu=0.13$, ... $\nu=0.1$, ___ $\nu=0.05$; $T=106$ K, $\nu=0.05$, _ _ _ _.

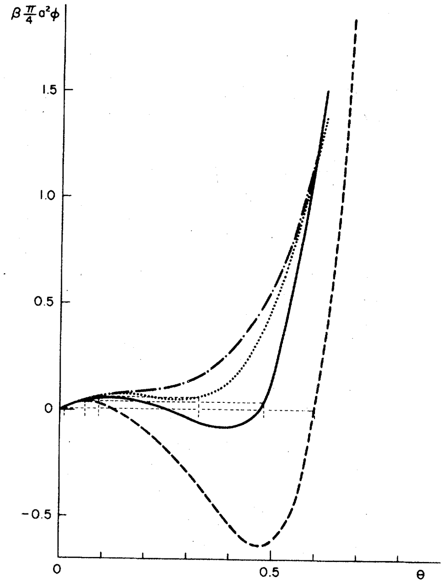

FIG. 8. Adsorbate equation of state: reduced spreading pressure, $\beta a_0\phi$ as a function of coverage θ. Same parameters as in Fig. 7.

(a) The attractive forces of course reduce significantly the necessary bulk gas pressure for high coverages since they increase the cohesion energy between the adsorbed molecules. For the same reason, the spreading pressure of the complete system is much lower than the one for the reference system.

(b) Of particular interest, however, is the effect of the localization on the gas-liquid equilibrium as may be judged from the effect of the parameter ν (and $\Delta\epsilon$) on the critical parameters. Inspecting Fig. 8 we see that at given χ^a, ϵ/T and $\Delta\epsilon/T$ ratios the critical temperature decreases with ν.

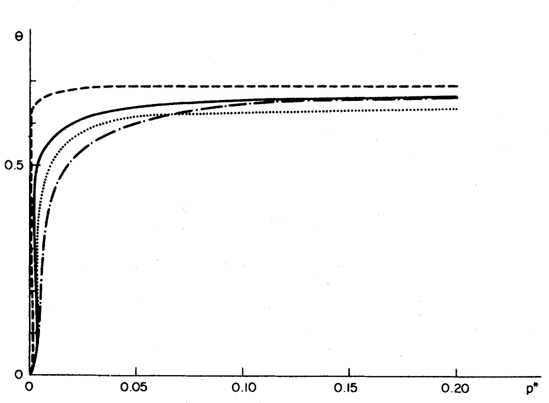

FIG. 9. Adsorption isotherm coverage θ as a function of reduced pressure p^*. Same parameters as in Fig. 7.

Note that this effect can easily be confused with the modification of the adsorbate-adsorbate intermolecular interaction by the substrate, that one may expect for other reasons, e.g., many-body forces in physisorption or renormalization in chemisorption.[17] These are two effects which make the adsorbate equation of state differ from the hypothetical two-dimensional bulk gas: localization and modification of the intermolecular potential by the substrate. The theoretical results on the importance of the later one and our present result on localization effects, make it appear very difficult to separate these two from the experimental data.

The inclusion of the attractive forces has a dramatic effect on the (configurational) isosteric heat (Figs. 10 and 11). The reason for this is that the "melting" of the localized molecules was a purely endothermic process in the reference system while now, in becoming mobile, the molecules also make better use of their attractive potential. In some extreme situations it may cause an increase of the isosteric heat with increasing θ. Such situations may occur either when the attraction between pairs of adsorbed molecules is very strong or when the barrier to lateral translation is relatively small.

The effect of temperature on the isosteric heat is much more complicated to interpret since temperature affects both the composition of the fluid and the law of interaction of the particles in the system. At high enough temperatures the system approaches the reference system and the isosteric heat falls off with the temperature because the localized particles "melt." At very low temperatures we may expect, since the attractive forces dominate the fluid, that the isosteric heat will increase with temperature as much as it does in the case of a density increase. This is not very evident, however, since it involves very low temperatures where the fraction of mobile particles is extremely small and thus not easy to treat. We would probably have to go to much lower ratios of $\Delta\epsilon/\epsilon$ to study these phenomena.

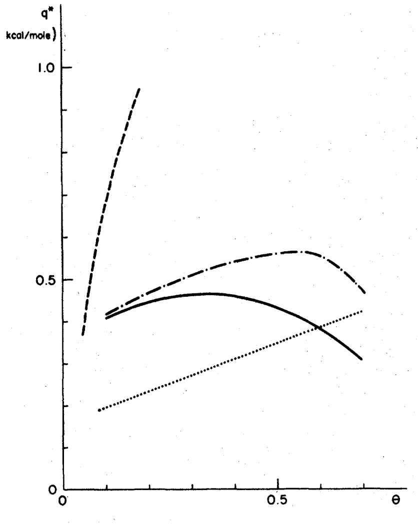

FIG. 10. Isosteric heat of adsorption, q^*, as a function of the coverage. Same parameters as in Fig. 8.

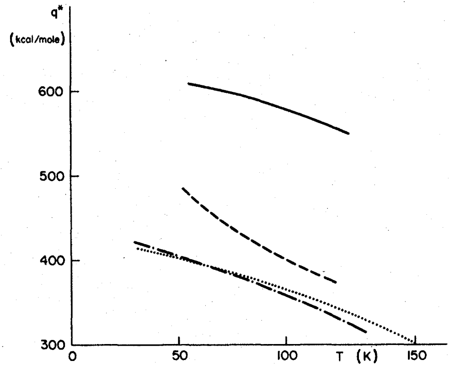

FIG. 11. Isosteric heat of adsorption, q^*, as a function of the surface temperature T; same parameters as in Fig. 8.

VIII. CONCLUSIONS

The complete adsorption isotherm of simple gases on inert solids[11] includes two separate regions of transition from an in-registry adsorbed gas to either a mobile or out-of-registry adsorbate. At low coverages (and low temperatures) the localized lattice-gas predominates and on increasing the bulk gas pressure a *gradual* transition to delocalized fluid occurs. This phenomena interferes with the gas-to-liquid phase transition at temperatures below the critical two-dimensional temperature. On the other hand at high coverages the in-registry solid adsorbate transforms *rather abruptly* into out-of-registry adsorbate. Both transitions can be considered as originating from nonadditivities in the hard-sphere diameters but, whereas, in the former region attractive forces play a dominant role (fluid-fluid transition) they have only a limited effect on the latter transition. The present model is thus appropriate for the description of the gradual transition from lattice gas to delocalized two-dimensional fluid and its interplay with fluid condensation. The Holland model[13,1] can handle the high-density "delocalization" (out-of-registry adsorbate) where phase transition takes place.

In addition, we are rather confident that SPT and other theories can handle the problem of a mixture of two kinds of polygons with nonadditive repulsive cores. In particular it would be interesting to solve the SPT for a mixture of (mobile) hard spheres and (localized) parallel hard squares (or other polygons) with nonadditive hard-core parameters. Steele[3a] developed more than a decade ago a theory for the partial localization of adsorbates based on the perturbation expansion, where he considered the pure hard-discs fluid as the reference state. Using the nonadditive hard-discs mixture as our reference state we could eliminate the expansion with respect to one parameter, namely, the barrier to lateral movement of the adsorbate—$\Delta\epsilon$.

An important aspect remained "unsolved," namely, the correct relation between adsorbent lattice parameters and the hard-sphere diameters of the model. The diameter of the Wigner-Seitz cell may be a suitable choice for physisorption systems, but we think for chemisorption only comparison with experiments and evidence from after observations like diffraction experiments can tell. In this case, like for liquid metals, scaled particle theory of nonadditive hard spheres may be used as an empirical concept to incorporate different coordination members.

ACKNOWLEDGMENT

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APPENDIX A: SOLUTIONS WITH DIFFERENT SCALE FUNCTIONS

In the previous work we had always obtained results with the following scale function:

$$a_{ij}\xi_{ij}(\lambda)=\tfrac{1}{2}(a_{ii}+a\Delta_{ij})\lambda + \tfrac{1}{2}(a_{jj}+a\Delta_{ij}),\quad i,j=l,m\,. \tag{A1}$$

It can indeed be shown, that Eq. (32) cannot be correct in the general case of nonadditive hard discs, since it does not give a correct macroscopic limit for additive discs. Equation (A1) would not suffer from this shortcoming. However, it is evident, and can be shown, that this problem of an incorrect additive limit does not exist for symmetric hard sphere interactions, $\nu=0$. Our mixture with $\Delta=-\frac{1}{2}\nu$, while nonsymmetric in general, becomes symmetric in the additive limit, $\Delta=0$. But since otherwise one has to use Eq. (A1) we give the results for this scale function. Following otherwise the procedure of Sec. IV, one finds

$$\bar{\lambda}_m=-\frac{\nu}{4-\nu}\,,\quad \bar{\lambda}_l=-\frac{\nu}{4+3\nu}\,. \tag{A2}$$

$$W_m^0=-kT\ln\left[1-x_m\theta\left(\frac{1-\nu/2}{1-\nu/4}\right)^2 - (1-x_m)\theta(1-\nu/4)^{-2}\right]. \tag{A3}$$

$$W_l^0=-kT\ln\left[1-x_m\theta\left(\frac{2-\nu^2}{2+3/2\nu}\right)^2 - (1-x_m)\theta\left(\frac{(1+\nu)(2+\nu)}{2+3/2\nu}\right)^2\right]. \tag{A4}$$

$$W_m^1=2kTe^{\beta W_m^0}\theta\,\frac{2(2-\nu)}{4-\nu}\,. \tag{A5}$$

$$W_l^1=2kTe^{\beta W_l^0}\frac{2+\nu}{4+3\nu}\,\theta[x_m(2-\nu^2) + 2(1-x_m)(1+\nu)^2]\,. \tag{A6}$$

But the macroscopic limit shows the major shortcoming of this scale function, the presence of a shell filled with a pure fluid of localized discs. This contradicts the physical fact that a mobile particle cannot distinguish between localized and mobile discs.

It can be shown analogously that the scale function,

$$\xi_{ij}(\lambda)=\tfrac{1}{2}(1+\lambda)\,, \tag{A7}$$

leads to the same result as the scale function Eq. (32).

APPENDIX B: REDUCTION OF THE VARIOUS INTEGRALS

We need the integral

$$I=\int\int d\zeta_3\,d\eta_3\,(e^{-\beta u^0(r_{13})}-1)(e^{-\beta u^0(r_{23})}-1). \tag{B1}$$

We will need this integral for different values of disc diameters and distances r. We start with the case of simple hard discs of diameter σ.

1. $\sigma_1=\sigma_2=\sigma$.

Introducing the variables u, v, and r we have,

$$d\zeta_3\,d\eta_3=\frac{v}{r}\sin^{-1}\left[\mathrm{arc\ cos}\left(\frac{u^2+r^2-v^2}{2ur}\right)\right]du\,dv\,, \tag{B2}$$

and thus

$$I=\frac{2}{r}\int_{r/2}^{\sigma}du\int_{r-u}^{u}v\,dv \times\sin^{-1}\left[\mathrm{arc\ cos}\left(\frac{u^2+r^2-v^2}{2ur}\right)\right] =\frac{2}{r}\int_{r/2}^{\sigma}du\int_{r-v}^{v}v\,dv\left[1-\left(\frac{u^2+r^2v^2}{2ur}\right)^2\right]^{-1/2}. \tag{B3}$$

The first integration can be carried out after a change of variables to

$$w=\frac{u^2+r^2-v^2}{2ur},$$

to lead to

$$I=-2\int_{r/2}^{\sigma} du\,u\left[\arcsin\left(\frac{r}{2u}\right)-\frac{\pi}{2}\right]. \tag{B4}$$

This integral can also be carried analytically making two successive partial integrations with changes in variables so that we arrive finally at

$$I(\sigma,r)=-r\sigma\left\{\frac{\sigma}{r}\arcsin\left(\frac{r}{2\sigma}\right)+\frac{1}{2}\left[1-\left(\frac{r}{2\sigma}\right)^2\right]^{1/2}\right\}+\frac{\pi}{2}\sigma^2,\qquad r<2\sigma. \tag{B5}$$

2. For different diameters we distinguish four situations, to the different possibilities of intersection:

(i) $\sigma_1+\sigma_2>r>\sigma_2>\sigma_1$.
(ii) $\sigma_2>r>\sigma_1$.
(iii) $\sigma_1>r>\sigma_2-\sigma_1$.
(iv) $\min(\sigma_1,\sigma_2-\sigma_1)>r>0$.

The last case is trivial and leads to

$$I(r,\sigma)=\frac{1}{2}\pi\sigma_1^2.$$

In case (i) we have

$$I^1(\sigma_1,r-\sigma_2;\sigma_2)=\frac{1}{r}\int_{r-\sigma_2}^{\sigma_1}du\int_{r-u}^{\sigma_2}dv\,v\left[1-\left(\frac{u^2+r^2-v^2}{2ur}\right)^2\right]^{-1/2}, \tag{B6}$$

which leads to the result

$$I^1(r,\sigma_1,\sigma_2)=\tfrac{1}{4}\pi(\sigma_1^2+\sigma_2^2)-\tfrac{1}{2}\sigma_1^2\arcsin\left(\frac{\sigma_1^2-\sigma_2^2+r^2}{2\sigma_1 r}\right)-\frac{1}{2}\sigma_2^2\arcsin\left(\frac{\sigma_2^2-\sigma_1^2+r^2}{2r\sigma_2}\right)-\frac{1}{2}r\sigma_2\left[1-\left(\frac{r^2+\sigma_2-\sigma_1^2}{2r\sigma_2}\right)^2\right]^{1/2}. \tag{B7}$$

In case (ii) we can write

$$I^2(r,\sigma_1,\sigma_2)=I_1^2(r,\sigma_1,\sigma_2)+I^1(\sigma_1,\sigma_2-r;\sigma_2), \tag{B8}$$

with

$$I_1^2(r,\sigma_1,\sigma_2)=\frac{1}{r}\int_0^{\sigma_2-r}du\int_{r-u}^{r+u}dv\,v\left[1-\left(\frac{u^2+r^2-v^2}{2ur}\right)^2\right]^{1/2}=-\tfrac{1}{2}\pi(\sigma_2-r)^2. \tag{B9}$$

For case (iii) we obtain the same result as in case (ii).

APPENDIX C: DETAILS OF THE PERTURBATION EXPANSION

The $g_{ij,\kappa}^{02}(r)$ can be expressed in terms of the following integrals:

$$I_{ij,kl}(r)=\frac{\pi}{4}(a_{ij}^2+a_{kl}^2)-\tfrac{1}{2}a_{ij}^2\arcsin\left(\frac{a_{ij}^2-a_{kl}^2+r^2}{2a_{ij}r}\right)-\frac{1}{2}a_{kl}^2\arcsin\left(\frac{a_{kl}^2-a_{ij}^2+r^2}{2ra_{kl}}\right)-\tfrac{1}{2}ra_{kl}\left[1-\left(\frac{r^2+a_{kl}^2-a_{ij}^2}{2a_{kl}r}\right)^2\right]^{1/2}. \tag{C1}$$

Note that this integral is symmetric towards permutations of (i,j) with (k,l). On the diagonal $i,j=k,l$, it degenerates to

$$I_{ij,ij}(r)=-a_{ij}^2\arcsin(r/2a_{ij})-(ra_{ij}/2)\left[1-\left(\frac{r}{2a_{ij}}\right)^2\right]^{1/2}+\frac{\pi}{2}a_{ij}^2. \tag{C2}$$

For the constituents of the radial distribution function one has

$$g_{mm,m}(r)=g_{mm,l}(r)=g_{ml,m}(r)=g_{ll,m}(r)=I_{mm,mm}(r), \tag{C3}$$

$$g_{ml,l}(r)=I_{mm,ll}(r), \tag{C4}$$

$$g_{ll,l}(r)=I_{ll,ll}(r). \tag{C5}$$

A. Thermodynamic properties

If we insert finally Eqs. (C3)–(C5) into Eqs. (48) and (49) we find for the perturbation terms

$$
\begin{aligned}
(\mu_m - \mu_m^0) = &+ \frac{\pi}{A} \int_a^\infty r\,dr\,\tilde{U}(r) 2N_m + \frac{2\pi N_l}{A} \int_a^\infty r\,dr\,\tilde{U}(r) \\
&+ \frac{\pi}{A} \int_a^{2a} r\,dr\,\tilde{U}(r) \frac{\partial}{\partial N_m}\left[N_m^2\left(\frac{N_m}{A} + \frac{N_l}{A}\right)\right] I_{mm,mm}(r) \\
&+ \frac{2\pi N_l}{A} \int_a^{2a} r\,dr\,\tilde{U}(r)\left[\frac{\partial}{\partial N_m}\left(N_m \frac{N_m}{A} I_{ll,ll}(r)\right)\right] \\
&+ \frac{2\pi N_l}{A} \int_a^{a(2+\nu)} r\,dr\,\tilde{U}(r)\left(\frac{\partial}{\partial N_m} N_m \frac{N_l}{A} I_{mm,ll}(r)\right).
\end{aligned}
\tag{C6}
$$

Or finally,

$$
\begin{aligned}
(\mu_m - \mu_m^0) = &+2\pi\theta \int_a^\infty r\,dr\,\tilde{U}(r) + 3\pi(\theta_m^2 + 2\theta_m\theta_l) \int_a^{2a} r\,dr\,\tilde{U}(r) I_{mm,mm}(r) \\
&+ 2\pi\theta_l^2 \int_a^{a(2+\nu)} r\,dr\,\tilde{U}(r) I_{mm,ll}(r).
\end{aligned}
\tag{C7}
$$

In the same way we find:

$$
\begin{aligned}
(\mu_l - \mu_l^0) = &+2\pi\theta_m \int_a^\infty dr\,r\tilde{U}(r) + 2\pi\theta_l \int_{a(1+\nu)}^\infty r\,dr\,\tilde{U}(r) + 2\pi\theta_m^2 \int_a^{2a} r\,dr\,\tilde{U}(r) I_{mm,mm}(r) \\
&+ 4\pi\theta_l\theta_m \int_a^{a(2+\nu)} dr\,r\tilde{U}(r) I_{mm,ll}(r) + 2\pi\theta_m\theta_l \int_{a(1+\nu)}^{2a} r\,dr\,\tilde{U}(r) I_{mm\ mm}(r) \\
&+ 3\pi\theta_l^2 \int_{a(1+\nu)}^{2a(1+\nu)} dr\,r\tilde{U}(r) I_{ll,ll}(r).
\end{aligned}
\tag{C8}
$$

And for Eq. (50)

$$
\begin{aligned}
(\phi - \phi^0) = &-\pi\theta_m^2 \int_a^\infty dr\,r\tilde{U}(r) - 2\pi\theta_m^2\theta \int_a^{2a} r\,dr\,\tilde{U}(r) I_{mm,mm}(r) - 2\pi\theta_m\theta_l \int_a^\infty dr\,r\,\tilde{U}(r) \\
&- 4\pi\theta_m^2\theta_l \int_a^{2a} dr\,r\,\tilde{U}(r) I_{mm,mm}(r) - 4\pi\theta_m\theta_l^2 \int_a^{a(2+\nu)} dr\,r\,\tilde{U}(r) I_{mm,ll}(r) \\
&- \pi\theta_l^2 \int_{a(1+\nu)}^\infty r\,dr\,\tilde{U}(r) - \pi\theta_m\theta_l^2 \int_{a(1+\nu)}^{2a} r\,dr\,\tilde{U}(r) I_{mm,mm}(r) \\
&- 2\pi\theta_l^3 \int_{a(1+\nu)}^{2a(1+\nu)} dr\,r\,\tilde{U}(r) I_{ll,ll}(r).
\end{aligned}
\tag{C9}
$$

For the calculation of the properties of the pure fluid in the cavity we will neglect interactions across the membrane but otherwise we use the same approximations that we have made in the bulk fluid; we thus have

$$
(\mu'_m - \mu_m^{0\prime}) = -2\theta'_m \int_a^\infty dr\,r\,\tilde{U}(r) - 3\pi(\theta'_m)^2 \int_a^{2a} r\,dr\,\tilde{U}(r) I_{mm,mm}(r),
\tag{C10}
$$

and

$$
(\phi'_m - \phi_m^{\prime 0}) = \pi(\theta'_m)^2 \int_a^\infty dr\,r\,\tilde{U}(r) - 2\pi(\theta'_m)^3 \int_a^{2a} dr\,r\,\tilde{U}(r) I_{mm,mm}(r).
\tag{C11}
$$

B. Integrals $J_{ii,jj}(\delta,\sigma)$ and $J_{ii,jj}(\delta,\sigma)$

The thermodynamic properties of our system are expressible through the following two integrals in the case of the square-well potential:

$$
J_{ii,jj}(\delta, \sigma) = \int_\sigma^\delta r\,dr\,I_{ii,jj}(r),
\tag{C12}
$$

and

$$J_{ii,ii}(\delta,\sigma)=\int_\sigma^\delta r\,dr\,I_{ii,ii}(r)\,. \tag{C13}$$

For these we find

$$J_{ii,ii}(\delta,\sigma)=-[\tfrac{1}{2}a_{ii}^2(r^2-a_{ii}^2)\operatorname{arc\,sin}(r/2a_{ii})+\tfrac{1}{16}r(4a_{ii}^2-r^2)^{1/2}(2a_{ii}^2+r^2)-\tfrac{1}{4}\pi a_{ii}^2r^2]_\sigma^\delta\,, \tag{C14}$$

and

$$J_{ii,jj}(\delta,\sigma)=[\tfrac{1}{8}\pi(a_{ii}^2+a_{jj}^2)r^2-\tfrac{1}{2}a_{ii}^2K_{ii,jj}-\tfrac{1}{2}a_{jj}^2K_{jj,ii}-\tfrac{1}{4}L_{ii,jj})]_\sigma^\delta\,, \tag{C15}$$

where

$$\begin{aligned}K_{ii,jj}&=\tfrac{1}{2}r^2\operatorname{arc\,sin}\left(\frac{a_{ii}^2-a_{jj}^2+r^2}{2a_{ii}r}\right)+\frac{1}{2}a_{jj}^2\operatorname{arc\,sin}\left(\frac{a_{ii}^2+a_{jj}^2-r^2}{2a_{ii}a_{jj}}\right)\\&\quad+\tfrac{1}{2}a_{ii}a_{jj}\left[1-\left(\frac{a_{ii}^2+a_{jj}^2-r^2}{2a_{ii}a_{jj}}\right)^2\right]^{1/2}.\end{aligned} \tag{C16}$$

$$\begin{aligned}L_{ii,jj}&=-\tfrac{1}{2}\Big[+\tfrac{1}{2}(a_{ii}^2+a_{jj}^2-r^2)[2r^2(a_{ii}^2+a_{jj}^2)-(a_{ii}^2-a_{jj}^2)^2-r^4]^{1/2}\\&\quad+2a_{ii}^2a_{jj}^2\operatorname{arc\,sin}\left(\frac{a_{ii}^2+a_{jj}^2-r^2}{2a_{ii}a_{jj}}\right)\Big].\end{aligned} \tag{C17}$$

One sees that $J_{ii,jj}$ becomes $J_{ii,ii}$ for $\nu=0$. In the case[15] of the noble gases $\chi\approx 1.85$, i.e., smaller than 2, and we can identify δ with the original upper limits from Eqs. (C6) to (C11).

In terms of reduced coordinates, $\tilde{r}=r/a$ and denoting the upper limit for the integrals by t, Eqs. (C14)–(C17) read:

$$J_{mm,mm}(t,1)=a^2[\tfrac{1}{2}(\tilde{r}^2-1)\operatorname{arc\,sin}(\tfrac{1}{8}\tilde{r}^2)-\tfrac{1}{4}\pi\tilde{r}^2+(2+r^2)]_1^t\,. \tag{C18}$$

$$\begin{aligned}J_{ll,ll}(t,1+\nu)&=\pi a^4\{\tfrac{1}{2}(1+\nu)^2[\tilde{r}^2-(1+\nu)^2]\operatorname{arc\,sin}\tfrac{1}{2}\tilde{r}\\&\quad-\tfrac{1}{4}\pi(1+\nu)^2\tilde{r}^2+\tfrac{1}{16}\tilde{r}[4(1+\nu)^2-\tilde{r}^2]^{1/2}\,[2(1+\nu)^2+\tilde{r}^2]\}_{1+\nu}^t\,.\end{aligned} \tag{C19}$$

$$J_{mm,ll}(t,1)=a^4\{\tfrac{1}{8}\pi[1+(1+\nu)\tilde{r}^2]-\tfrac{1}{2}K^*_{mm,ll}-\tfrac{1}{2}(1+\nu)^2K^{*2}_{ll,mm}-\tfrac{1}{4}L^*_{mm,ll}\}_1^t\,. \tag{C20}$$

$$\begin{aligned}K^*_{mm,ll}&=\frac{\tilde{r}^2}{2}\operatorname{arc\,sin}\left(\frac{\tilde{r}^2-2\nu-\nu^2}{2\tilde{r}}\right)+\frac{1}{2}(1+\nu)^2\operatorname{arc\,sin}\left(\frac{2+2\nu+\nu^2-\tilde{r}^2}{2(1+\nu)}\right)+\frac{1+\nu}{2}\\&\quad\times\left[1-\left(\frac{2+2\nu+\nu^2-\tilde{r}^2}{2(1+\nu)}\right)^2\right]^{1/2}.\end{aligned} \tag{C21}$$

$$\begin{aligned}L^*_{mm,ll}&=-\tfrac{1}{4}(2+2\nu+\nu^2-\tilde{r}^2)[2\tilde{r}^2(2+2\nu+\nu^2)-\nu^2(2+\nu)^2-\tilde{r}^4]^{1/2}\\&\quad-2(1+\nu)^2\operatorname{arc\,sin}\left(\frac{2+2\nu+\nu^2-\tilde{r}^2}{2(1+\nu)}\right).\end{aligned} \tag{C22}$$

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