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Static structure of the two-dimensional hard-disk plus Yukawa fluid

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The static structure of the two-dimensional hard-disk plus Yukawa fluid is studied on the basis of the hypernetted chain approximation. We find that the most relevant features exhibited by the three-dimensional hard-sphere plus Yukawa system are also exhibited by its two-dimensional counterpart.

I. INTRODUCTION

The study of liquid systems is an important area of chemical physics. Their static and dynamic properties have been the subject of extensive reviews, even at the textbook level.[1,2] Starting from the simplest model (a "simple liquid," i.e., a monocomponent system of spherical particles), the theoretical and experimental study of liquids has expanded to include increasingly more complex systems and conditions (liquid mixtures, molecular fluids, inhomogeneous liquids, etc.). This is also illustrated by the progress achieved in the understanding of the basic static and dynamic properties of colloidal dispersions, which, to a large extent, has been based on a rather straightforward translation of theoretical and experimental approaches developed in the context of atomic liquids.[3–6] One of the most provoking aspects of these developments is the availability of colloidal models that are believed to represent at the mesoscopic level what occurs at atomic length and time scales.[5–14] Although the dynamic properties of colloidal systems do exhibit intrinsic differences with respect to atomic liquids (Brownian motion, hydrodynamic interactions, etc.), the study of the static properties of model colloidal suspensions has provided an additional field of application of otherwise fairly well established concepts of the statistical thermodynamics of liquids. Current frontiers of these developments are, for instance, the study of colloidal mixtures,[6–8] colloidal glasses,[9] dispersions of anisotropic particles,[10,11] colloidal systems in the presence of external fields,[12–14] etc.

Recently, attention has been given to the dependence on dimensionality of the structural and dynamic properties of colloidal systems, with emphasis in understanding the most salient differences between two- and three-dimensional systems concerning their phase behavior, static structure, dynamic properties, etc.[13] In an attempt to contribute to this direction of research, in this work, we analyze the main features of the static structure of a two-dimensional hard-disk plus Yukawa fluid as compared with its three-dimensional counterpart. In Sec. II, we summarize the basic concepts concerning the model of the interactions between particles considered in this work, and the theoretical approach we employ to calculate its static structure. In Sec. III, we present our results for the radial distribution function and the static structure factor, as obtained from the hypernetted chain (HNC) and Percus–Yevick (PY) approximations. In Sec. IV, we summarize and discuss the main features of these structural properties.

II. THEORY

Here we are concerned with the calculation of the radial distribution function and the static structure factor of a two-dimensional system of particles interacting via a hard-core plus repulsive Yukawa pair potential

$$\beta u(r)=Ke^{-z[(r/\sigma)-1]}/(r/\sigma), \quad \frac{r}{\sigma}>1$$

$$=\infty, \quad \frac{r}{\sigma}<1 \qquad (1)$$

at temperature $T[=(k_B\beta)^{-1}$, k_B being Boltzmann's constant] and number concentration n, with σ being the particle diameter. This dimensionless form of the pair potential has played an important role in the study of three-dimensional suspensions of highly charged colloidal particles. In such case, it corresponds to the screened Coulomb effective pair potential, and upon an adequate definition of K and z, it corresponds to the well-known Derjaguin–Landau–Verwey–Overbeek (DLVO) effective potential.[15,16] This, however, is not the basic reason why we choose this model potential in this study, since there is no similar physical basis for this potential to represent a specific real two-dimensional system (although it may constitute a reasonable zeroth-order representation of the effective interaction between two highly charged colloidal particles in an effectively two-dimensional suspension confined between two parallel charged walls.[13,14] In reality, our choice of this model potential for our two-dimensional study is rather arbitrary. This is justified because we are not interested in studying the properties of a real two-dimensional system in particular. This would require a careful analysis of the actual form of the effective pair interaction between particles, and no prototypical two-dimensional model experimental system is available for which such analysis has been carried out. As mentioned above, the hard-sphere plus repulsive Yukawa model has already been studied extensively in the context of three-dimensional systems. Thus, studying the same model in two dimensions will allow us to exhibit the effects of dimensionality on some of its properties, as we do below.

Our calculation of the structural properties will be based on the solution of the Ornstein–Zernike (OZ) integral equation

$$h(r)=c(r)+n\int h(|\mathbf{r}-\mathbf{r}'|)c(r')d^2r' \quad (2)$$

within the HNC closure

$$c(r)=-\beta u(r)+h(r)-\ln[1+h(r)]. \quad (3)$$

In this equation, $h(r)$ and $c(r)$ are, respectively, the total and the direct correlation functions. We shall also compare, however, with the results of the PY closure

$$c(r)=g(r)(1-e^{\beta u(r)}) \quad (4)$$

in which $g(r)=h(r)+1$ is the radial distribution function. In the numerical solution of the resulting integral equations, we followed the method of Lado.[17] In what follows, we describe the results of these calculations.

III. RESULTS

We have explored the parameter space of our system by choosing representative values of the dimensionless parameters K, z, and $n^*(\equiv n\sigma^2)$. We start from the region where one may be confident that the fluid is indeed the thermodynamically stable phase of the system. Here we study the case of weakly screened potentials ($z=0.15$). In Fig. 1, we illustrate the effect of increasing the coupling parameter K at fixed density ($n^*=0.003$) on the static structure factor [Fig. 1(a)] and on the corresponding radial distribution function [Fig. 1(b)]. The first interesting observation is that for highly coupled systems [$K=500$ and 1000 in Fig. 1(a)], the main effect of increasing K is to emphasize the structure, represented by the height of the peaks of $S(k)$, without a considerable shift in the position of the main peak. Thus, just as in the corresponding weakly screened-highly coupled three-dimensional case,[3,18] the position of the first maximum of $S(k)$, $k_{\max}$, only depends, to a first approximation, on the particle concentration n^*. Deviations are observed, as expected, at smaller couplings [illustrated in Fig. 1(a) by curve $K=100$]. The dependence of $k_{\max}$ on n^* is discussed later on. In a similar manner, Fig. 1(b) illustrates the dependence of $g(r)$ on K, at fixed z and n^*. From this figure, we notice that a strong, but weakly screened Yukawa repulsion defines an effective distance of closest approach between two particles σ' [the distance from $r=0$ to the point where $g(r)$ departs appreciably from zero]. This effective diameter σ' increases with K [in Fig. 1(b), σ' is approximately 6σ, 10σ, and 12σ for $K=100$, 500, and 1000, respectively]. Besides this effect, the main consequence on $g(r)$ of increasing K is an increase on the structure represented by the height of its first and subsequent maxima without little change in their position. Let us mention that the presence of an effective diameter σ' larger than σ indicates that the structure is determined only by the Yukawa tail, and not by the real diameter. As we see below, this leads to a "rescaling" property of the structure of our model, equivalent to the physical rationale upon which the rescaled mean spherical approximation (RMSA) for the corresponding three-dimensional system was constructed.[18,19]

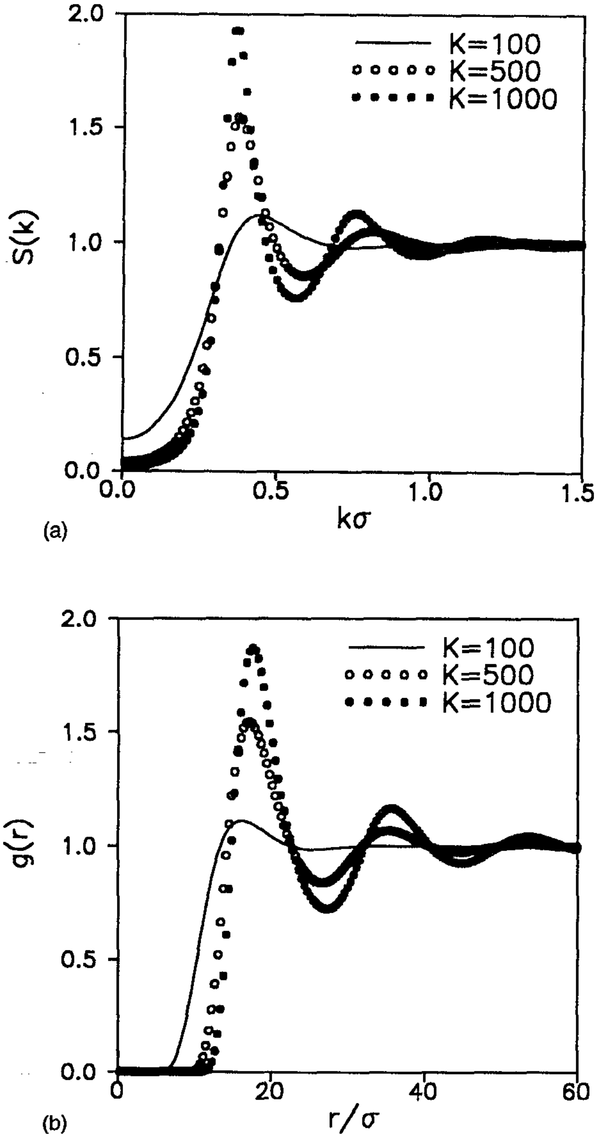

FIG. 1. (a) Static structure factor and (b) radial distribution function of the two-dimensional hard-disk plus Yukawa fluid of reduced density $n^*=0.003$, screening constant $z=0.15$, and Yukawa amplitude $K=100$ (solid line), 500 (open circles), and 1000 (closed circles). As it is observed, increasing the interaction between particles, at fixed concentration, increases the local structure of the system without an appreciable change in the position of the first maximum.

Figure 2 complements Fig. 1 and illustrates the dependence of the structure on particle concentration at fixed $z(=0.15)$ and $K(=500)$. As observed in Fig. 2(a) increasing n^* leads to the expected increase in the structure, but this time involving a shift of the position of the maxima of $S(k)$ to larger wave vectors. The corresponding changes in $g(r)$ are illustrated in Fig. 2(b), where one can see that the effective diameter σ' decreases, as expected, when the system is compressed. Concerning the dependence of $k_{\max}$ on n^*, which for strongly coupled three-dimensional systems is proportional to $2\pi/l$, l being the mean interparticle

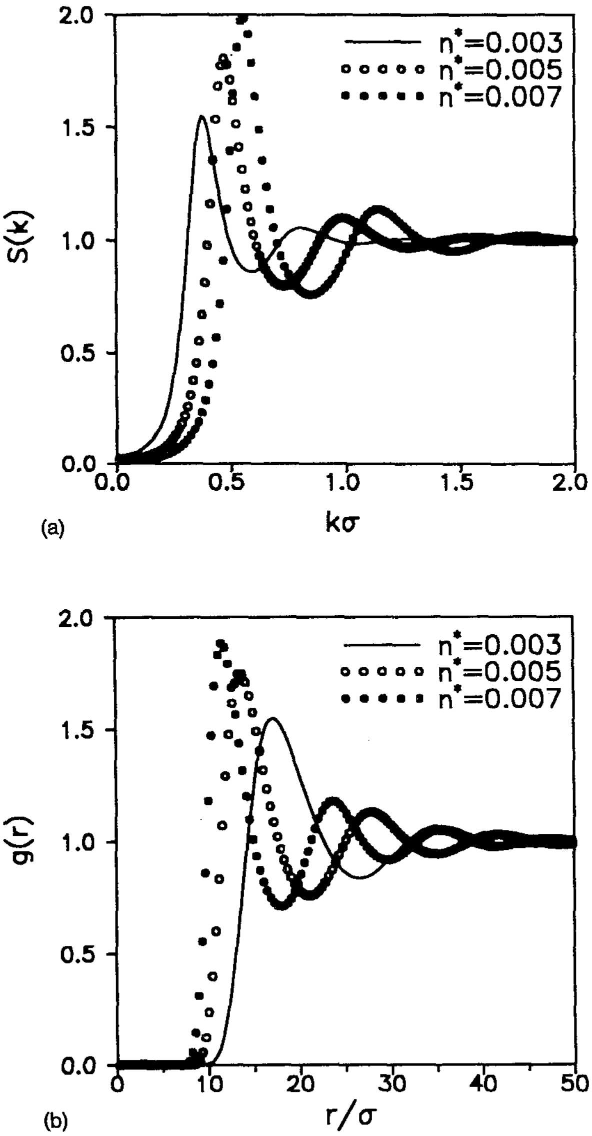

FIG. 2. (a) The effect on the static structure factor and (b) on the radial distribution function of increasing the reduced density n^* at fixed screening constant $z=0.15$ and Yukawa amplitude $K=500$.

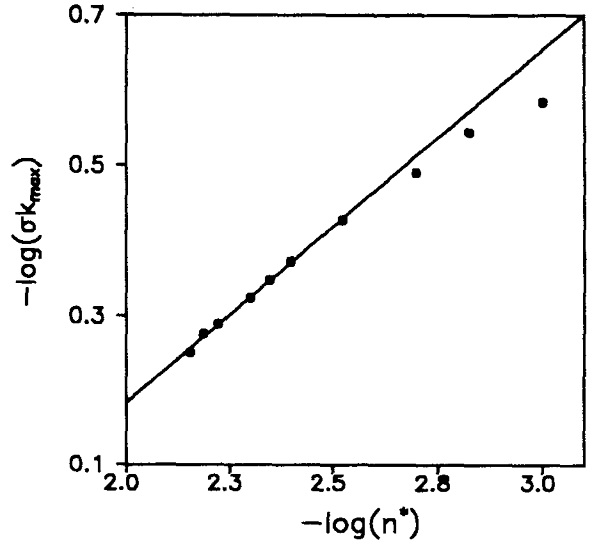

FIG. 3. $(k_{max}\sigma)$ as a function of reduced density (n^*) for $z=0.15$ and $K=500$, according to HNC (solid circles). The straight line (of slope 0.47) is a linear regression fit of the HNC results for $n^*>0.002$. The small statistical dispersion of the HNC results is due to numerical errors.

distance $l=n^{-1/3}$,[20,21] we find a corresponding behavior for our two-dimensional system. This is illustrated in Fig. 3, where we plot $-\log(\sigma k_{max})$ vs $-\log(n^*)$. If k_{max} follows a power law of the form $k_{max}=cn^s$, then the plot in Fig. 3 should be a straight line of slope s. Except for the three lowest concentrations considered in the figure ($n^*=0.001$, 0.0015, and 0.002), our HNC results follow a straight line of slope $s=0.47$, and the intercept leads to a value of 5.74 for the proportionality constant c. Thus, we see that for the coupling parameter $K=500$, already for $n^*>0.002$, our HNC results for k_{max} follow rather closely the expected dependence on concentration, given by $k_{max}=2\pi/l$, where $l=n^{-1/2}$, in the regime where the strong Yukawa repulsion dominates the structure.

Thus far, all of the features we have highlighted on the structure of our two-dimensional system can be said to be expected on the basis of what we know about its three-dimensional counterpart. At least, this is what our HNC results reveal, and we expect that this conclusion will eventually be confirmed by other theories and/or computer simulations. For the moment, it is interesting to notice that the PY closure leads to qualitative results similar to those we have described, although within differences in their quantitative results. In Fig. 4, we illustrate the magnitude of these quantitative differences.

Although the general scenario of the structure of the two-dimensional hard-disk plus Yukawa fluid is qualitatively similar to the corresponding three-dimensional system, it is also interesting to contrast the structure of the same system in two and three dimensions in a more direct manner. This can be done by comparing our results for the two-dimensional system with given values of K, z, and n^*, with a three-dimensional system with the same coupling and decay parameters, but with a value of n^* that corresponds to the same mean interparticle distance l as the two-dimensional system. This is done within the HNC approximation in Fig. 5. In this figure, we compare $g(r)$ for a two-dimensional system with $K=1000$, $z=0.15$, and $n^*=0.003$ (corresponding to $l=n^{-1/2}=18.26\sigma$) with the corresponding result for a three-dimensional system with the same K, z, and l (i.e., with $n^*=n\sigma^3=0.000\,164\,3$). As we see from this figure, in both cases, the effective hard-core diameter σ' is roughly the same ($\approx 12\sigma$), but the two-dimensional fluid is considerably more structured than its three-dimensional counterpart.

Concerning the effective hard-disk diameter σ', let us also mention that our two-dimensional system exhibits the same rescaling property observed in three dimensions. This property is illustrated in Fig. 6, where we plot the HNC radial distribution functions for three different sets of parameters (K, z, n^*), namely (a) (500, 0.15, 0.007); (b) (79.7, 0.6, 0.112); and (c) (39.36, 0.9, 0.252). The radial

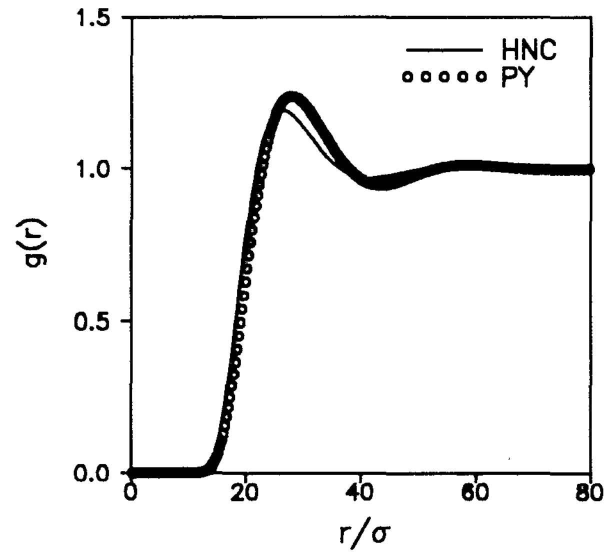

FIG. 4. A comparison of the radial distribution function of a two-dimensional hard-disk plus Yukawa fluid as calculated using the HNC (solid line) and PY (open circles) approximations for $K=500$, $z=0.15$, and $n^*=0.001$.

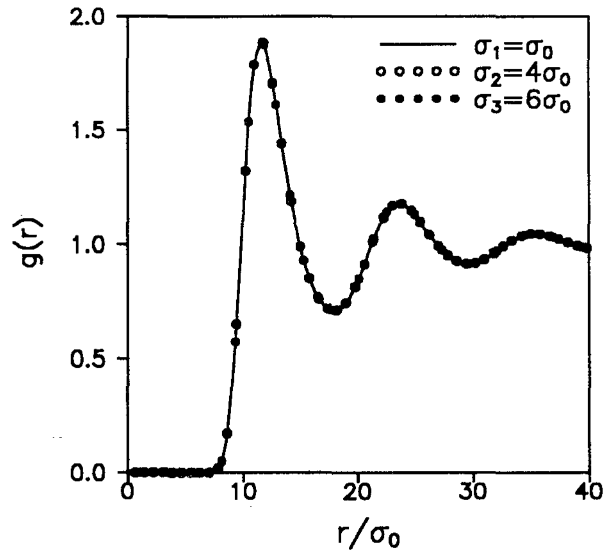

FIG. 6. The radial distribution function of the hard-disk plus Yukawa fluid for the following three different sets of dimensionless parameters (K, z, n^*): (a) (500, 0.15, 0.007) (solid line); (b) (79.7, 0.6, 0.112) (open circles); and (c) (39.36, 0.9, 0.252) (solid circles) plotted as a function of the dimensionless distance r/σ_0. These systems differ only in their hard-disk diameters σ, which are, respectively, σ_0, $4\sigma_0$, and $6\sigma_0$.

distance r is expressed in the same (arbitrary) unit length σ_0 in the three cases. Plotted in this manner, the radial distribution function for these three systems collapse onto a single curve. The reason for this is the following: The three systems correspond to the same number density n, the same coupling parameter $A \equiv K\sigma e^{z}$, and screening constant $\kappa \equiv z/\sigma$, but to different hard-disk diameter σ [$=\sigma_0$, $4\sigma_0$, and $6\sigma_0$, for (a), (b), and (c), respectively]. If the average kinetic energy (k_BT) is small enough so that $\beta u(\sigma)$ is large, it is quite unlikely that two particles approach each other to distances comparable to σ. Instead, there will be an effective distance of closest approach σ', which only depends on the Yukawa tail and not on the true diameter. Thus, two systems which have the same Yukawa tail (i.e., the same A and κ) and the same number concentration n, but differ only in their true diameter σ, will have essentially identical structure, and this is the situation illustrated in Fig. 6. Of course, the dimensionless parameters K, z, and n^* will be different because the true diameter is different. In three dimensions, the corresponding observation was employed in the construction of the so-called rescaled mean spherical approximation (RMSA),[19] which exploits the availability of an analytical solution of the mean spherical approximation (MSA)[22] for the three-dimensional hard-sphere plus Yukawa fluid. The resulting RMSA approximation has been of considerable value in the study of three-dimensional suspensions.[5,18] Unfortunately, no analytic solution is known for the MSA in two dimensions and this prevents the corresponding extension of the RMSA. Our interest in exhibiting this property in our two-dimensional HNC results derives, however, from its intrinsic interest. Furthermore, it is also interesting to note that this rescaling property is expected to be observed in the *exact* radial distribution functions and not necessarily in the results of an approximate theory such as HNC. Thus, observing this level of quantitative precision in the prediction of the HNC approximation provides additional confidence on its general accuracy.

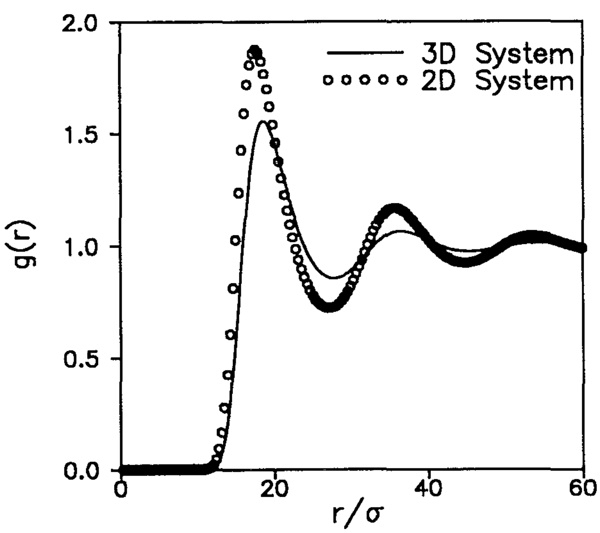

FIG. 5. The radial distribution function of the hard-disk and the hard-sphere plus Yukawa fluids, as calculated within the HNC approximation, for a Yukawa amplitude $K=1000$, screening constant $z=0.15$, and $n^*=n\sigma^2=0.003$ [two dimensions (open circles)] and $n^* = n\sigma^3=1.64 \times 10^{-4}$ [three dimensions (solid line)]. The mean interparticle distance in both cases is 18.26σ.

IV. CONCLUSIONS

In summary, we have shown that the description of the structural properties of the two-dimensional hard-disk plus Yukawa fluid provided by the HNC approximation presents a general picture not too different from its three-dimensional counterpart. Let us mention, however, that a theory like the HNC approximation, based on the Ornstein–Zernike equation, is devised explicitly to describe a structurally homogeneous and isotropic fluid. Thus, from results like the ones we have shown, nothing can be said concerning the existence of the hexatic phase separating the fully disordered fluid phase from the ordered solid phase.[13] It is possible that for some of the values of the parameters K and n^*, particularly at large couplings (large K and/or n^*), the most stable phase is no longer the fluid phase described here. However, this will have to be analyzed with the assistance of other theoretical methods, and not only with integral equation methods like the ones we have employed. Finally, let us make a brief comment concerning the numerical approach we employed in the solution of the HNC-OZ equation. As said before, our numerical calculations were based on Lado's method explained in Ref. 17. This is a direct iteration method, whose convergence is increasingly more difficult as the fluid becomes more structured (increasing K and/or n^*). We found that at fixed K, the method failed to converge at a certain concentration n^*, which depends on K (and, of course, on z, when we vary this parameter). It is interesting that the boundary of the region of convergence of this method, for $z=0.15$, and at large values of $K(\geqslant 500)$ was such that the effective packing fraction $n' \equiv n\sigma'^2$, where σ' is the effective hard-core diameter, was of the order of 0.45. It is also interesting to note that in this region, another "rescaling" property, not directly related to the one described before, seems to hold. This rescaling property consists of an almost exact superposition of the radial distribution function of systems with different K and n^*, but with the same effective packing fraction n', when $g(r)$ was plotted as a function of (r/σ'). This might indicate that in this regime (large K and/or n^*), the structure becomes rather hard-disk-like, in such a manner that the effective packing fraction n' is the most relevant parameter determining the structure of a highly coupled Yukawa fluid. This, and other issues, together with the analysis of the actual quantitative accuracy of the HNC approximation for two-dimensional fluids, will have to be studied in detail by comparing with other theories and with computer simulations. Our results presented here, however, constitute a first step in this direction.

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