MOLECULAR PHYSICS, 1987, VOL. 60, NO. 1, 113–119

# Critical behaviour of an adhesive-hard-sphere model in the mean spherical approximation

by J. J. BREY and A. SANTOS
Departamento de Física Teórica, Universidad de Sevilla,
Apdo. Correos 1065, Sector Sur, 41080 Sevilla, Spain
and F. CASTAÑO
Departamento de Termodinámica, Facultad de Ciencias,
Universidad de Extremadura, Avda. de Elvas,
06071 Badajoz, Spain

(*Received 30 June 1986; accepted 15 August 1986*)

Starting from the exact solution of the mean spherical approximation for the hard core Yukawwa potential, the limit of adhesive hard spheres (i.e. an infinitely strong attractive well with a depth related to the range, which goes to zero, by a power law) is analysed. It is shown that only one choice of the scaling power leads to a model with nontrivial interactions. A critical point is obtained which has spherical model values of the critical exponents, indicating that a singular role is not played by the adhesive-hard-sphere limit.

## 1. INTRODUCTION

In the last few years, a great deal of work has been devoted to the description of the critical region as predicted by integral equations for fluids. In most of the cases, this study has required the use of numerical methods, and it seems [1] that methods much more powerful than those currently available are needed in order to get reliable information very near the critical point. For this reason, few definitive numerical results have been established so far. It is then natural to take advantage of the existence of exact solutions exhibiting critical behaviour. In particular, there exists a solution of the Percus–Yevick (PY) approximation

$$c(r) = [1 - \exp(\phi(r)/k_B T)][1 + h(r)] \tag{1}$$

for the so-called adhesive-hard-sphere (AHS) model, defined through the interaction potential [2, 3]

$$\phi(r) = \lim_{d\to 0} \begin{cases} \infty, & r < \sigma, \\ k_B T \ln(12\tau d/\sigma), & \sigma < r < \sigma + d, \\ 0, & r > \sigma + d, \end{cases} \tag{2}$$

where $\tau$ is a dimensionless temperature-dependent parameter, $k_B$ is the Boltzmann constant, and $T$ is the temperature. The direct correlation function $c(r)$ and the total correlation function $h(r)$ are related through the Ornstein–Zernike equation

$$h(r) = c(r) + \rho \int d\mathbf{s}\, c(s) h(|\mathbf{r} - \mathbf{s}|), \tag{3}$$

$\rho$ being the number density.

The above model has been solved exactly [2], and, from the compressibility equation of state, the existence of a critical point has been shown. In addition, the critical exponents take classical values (e.g. $\gamma = 1$, $\delta = 3$). However, the critical behaviour does not correspond to a mean field theory, since the equation of state in the critical region does not have the classical form [3]. Let us remark that the possibility of solution of the model is based on the limit indicated in (2). In other words, no exact solution of the PY equation is known for a square well potential with finite width and depth.

Another quite well studied integral equation is the mean spherical approximation (MSA), given by the closure

$$\left.\begin{aligned} h(r) &= -1, & r<\sigma,\\ c(r) &= -\phi(r)/k_B T, & r>\sigma. \end{aligned}\right\} \tag{4}$$

This equation has been solved [4] and analysed in considerable detail [5] for the case of a three-dimensional fluid with a hard core Yukawa (HCY) potential,

$$\phi(r) = \begin{cases} \infty, & r<\sigma,\\ -\dfrac{J}{r/\sigma}\exp\left(-z\,\dfrac{r-\sigma}{\sigma}\right), & r>\sigma. \end{cases} \tag{5}$$

Here, $J$ is the depth of the attractive well, and $z$ is a parameter characterizing the range of the potential. For this model, the compressibility equation of state reads [5]

$$\chi^{-1} \equiv \frac{1}{k_B T}\left(\frac{\partial p}{\partial \rho}\right)_T = a^2 = \left[\frac{-CK + G\lambda + H\lambda^2}{F\lambda}\right]^2, \tag{6}$$

where $p$ is the pressure and $\lambda$ is a function of the reduced density $\eta \equiv (\pi/6)\rho\sigma^3$ while $K \equiv J/k_B T$: this function is given by the smallest real root of the quartic equation

$$-36\eta^2\lambda^4 + X\lambda^3 - 12\eta K\lambda^2 + DK\lambda - K^2 = 0. \tag{7}$$

Finally, in (6) and (7), $C$, $D$, $F$, $G$, $H$, and $X$ are functions of $\eta$, whose explicit expressions can be found in the Appendix of [5]. Of course, they depend parametrically on $z$.

The analysis of (6) and (7) shows [5] that, at a given $z$, there exists a spinodal line (loci of $a = 0$) in the $\eta - K$ plane having a minimum at the critical point $(\eta_c, K_c)$. Moreover, in the region enclosed by the spinodal line there is a line bounding a region where (7) fails to have real roots. This leads one to distinguish three regions in the $\eta - K$ plane [6]: points lying outside the spinodal line (Region I), points where there is no real solution (Region III), and points located between the spinodal line and the curve representing the limit of real solutions (Region II). The quantity $a$ is continuous in Regions I and II. In particular, it is analytic at the critical point, where, in addition, $\partial a/\partial\eta = 0$. As a consequence, the spherical model values of the critical exponents ($\gamma = 2$, $\delta = 5$) are obtained. Although these values differ from those usually referred to as classical, they are consistent with the mean field condition of analyticity of the free energy at the critical point [7].

Thus, the two models that we have just described lead to a quite different critical behaviour. A main point in the study of integral equations is to elucidate whether this kind of discrepancy is due to the equation itself or to the interaction potential considered. The apparent common features of the PY and MSA closures led Cummings and Stell [5] to conjecture that, at least for short-ranged potentials, the spherical model values of the critical exponents should also hold for the PY approximation. So, one could 'regard the quite different adhesive-sphere exponents in the PY approximation as stemming from the highly singular nature of that potential, which includes an attractive interaction that is infinitely strong and short ranged' [5].

However, there is some strong analytical [8] and also numerical [9] evidence indicating that the MSA and the PY approximation have an intrinsically different critical behaviour. In this paper, we also argue in that direction by studying an adhesive-hard-sphere limit in the MSA. This limit is introduced by starting from the HCY potential given in (5). We obtain spherical model values for the critical exponents, and, therefore, there does not seem to be anything singular in the AHS limit. This result suggests that the MSA and the PY approximation generally lead to quite different critical behaviour.

## 2. Adhesive-hard-sphere limit

The AHS potential given by (2) is defined as a square well potential in the limit of zero width and infinite depth. Of course, some relation between both limits is introduced in order to get something different from pure hard spheres or an unphysical infinitely strong attraction.

Our aim is to define a limit of the HCY potential leading to an interaction analogous to AHS. Then, we consider the potential (5) in the limit $z \to \infty$, $J \to \infty$, with the scaling relation

$$\tilde{J} = J/z^{\mu} = \text{finite}, \tag{8}$$

where $\mu$ is a nonnegative exponent to be determined in the following. From the explicit expressions given in [5], one easily gets

$$C = 12\eta \frac{1 + 2\eta}{(1 - \eta)^2} z^{-1} + O(z^{-2}), \tag{9}$$

$$D = z + O(z^0), \tag{10}$$

$$F = -6\eta + O(z^{-1}), \tag{11}$$

$$G = 6\eta \frac{1 + 2\eta}{(1 - \eta)^2} + O(z^{-1}), \tag{12}$$

$$H = 72 \frac{\eta^2}{1 - \eta} + O(z^{-1}), \tag{13}$$

$$X = 36\eta^2 \frac{2 + \eta}{(1 - \eta)^2} z^{-1} + O(z^{-2}). \tag{14}$$

As discussed in § 1, the main physical information is provided by the smallest real root of (7). Let us write

$$\tilde{\lambda} = \lambda/z^{\theta}, \tag{15}$$

where $\theta$ is a (positive or negative) exponent depending on $\mu$, and $\tilde{\lambda}$ cannot be either zero or infinity. Thus, (6) and (7) become

$$\chi^{-1} = \left[2\,\frac{1+2\eta}{(1-\eta)^2}\,\frac{\tilde{K}}{\tilde{\lambda}}\,z^{\mu-\theta-1} - \frac{1+2\eta}{(1-\eta)^2} - 12\,\frac{\eta}{1-\eta}\,\tilde{\lambda}z^{\theta}\right]^2, \tag{16}$$

$$-36\eta^2\tilde{\lambda}^4 z^{4\theta} + 36\eta^2\,\frac{2+\eta}{(1-\eta)^2}\,\tilde{\lambda}^3 z^{3\theta-1} - 12\eta\tilde{K}\tilde{\lambda}^2 z^{2\theta+\mu} + \tilde{K}\tilde{\lambda}z^{\theta+\mu+1} - \tilde{K}^2 z^{2\mu} = 0. \tag{17}$$

respectively, where we have introduced $\tilde{K} \equiv \tilde{J}/k_B T$. Since $\tilde{\lambda}$ must be finite, the leading terms in (17) have to be of order $z^{2\mu}$. Then, the following possibilities arise:

$$4\theta = 2\mu \geqslant \max\,(3\theta - 1,\ 2\theta + \mu,\ \theta + \mu + 1), \tag{18a}$$

$$3\theta - 1 = 2\mu \geqslant \max\,(4\theta,\ 2\theta + \mu,\ \theta + \mu + 1), \tag{18b}$$

$$2\theta + \mu = 2\mu \geqslant \max\,(4\theta,\ 3\theta - 1,\ \theta + \mu + 1), \tag{18c}$$

$$\theta + \mu + 1 = 2\mu \geqslant \max\,(4\theta,\ 3\theta - 1,\ 2\theta + \mu). \tag{18d}$$

The case (18 *b*) can be discarded, since $\mu$ is nonnegative. The cases (18 *a*) and (18 *c*) are equivalent and yield

$$\mu \geqslant 2, \quad \theta = \tfrac{1}{2}\mu. \tag{19}$$

Finally, the relation (18 *d*) is verified when

$$\mu \leqslant 2, \quad \theta = \mu - 1. \tag{20}$$

Let us analyse the allowed possibilities. If $\mu > 2$, (17) reduces to

$$-36\eta^2\tilde{\lambda}^4 - 12\eta\tilde{K}\tilde{\lambda}^2 - \tilde{K}^2 = 0, \tag{21}$$

which has the imaginary solutions $\tilde{\lambda} = \pm i\,(\tilde{K}/6\eta)^{1/2}$. Thus, no physical solution is obtained in this case, i.e. Region III fills the whole $\eta - \tilde{K}$ plane. The corresponding isothermal compressibility is given by

$$\chi^{-1} = -24\,\frac{\eta}{(1-\eta)^2}\,\tilde{K}z^{\mu}, \tag{22}$$

which diverges to $-\infty$ when $z \to \infty$.

For $\mu = 2$, we have

$$-36\eta^2\tilde{\lambda}^4 - 12\eta\tilde{K}\tilde{\lambda}^2 + \tilde{K}\tilde{\lambda} - \tilde{K}^2 = 0. \tag{23}$$

A simple analysis shows that this equation has real roots only when $\eta\tilde{K} \leqslant 9/512$. (In particular, on the boundary line $\eta\tilde{K} = 9/512$, the double real root is $\tilde{\lambda} = 16\tilde{K}/9$.) So, in this case, there exists a Region II, where

$$\chi^{-1} = \left(\frac{12\eta}{1-\eta}\right)^2 \tilde{\lambda}^2 z^2, \tag{24}$$

that goes to $+\infty$ when $z \to \infty$. In Region III, defined by $\eta\tilde{K} > 9/512$, (24) still holds, but $\tilde{\lambda}$ is now complex.

Summary of the main results obtained in the text for the different values of the scaling exponent $\mu$.

| Value of $\mu$ | Value of $\theta$ | Regions in the $\eta - \tilde{K}$ plane | Inverse isothermal compressibility |
|---|---|---|---|
| $0 < \mu < 1$ | $\mu - 1$ | Region I | Hard spheres |
| $\mu = 1$ | 0 | Region I | |
| | | Region II | Adhesive hard spheres |
| $1 < \mu < 2$ | $\mu - 1$ | Region II | Real, positive, divergent |
| $\mu = 2$ | 1 | Region II | Real, positive, divergent |
| | | Region III | Complex, divergent |
| $\mu > 2$ | $\frac{1}{2}\mu$ | Region III | Real, negative, divergent |

Let us now consider $0 \leqslant \mu < 2$. Then, (17) becomes

$$\tilde{K}\tilde{\lambda} - \tilde{K}^2 = 0, \tag{25}$$

whose solution is $\tilde{\lambda} = \tilde{K}$. Substitution into (16) yields

$$\chi^{-1} = \left[\frac{1 + 2\eta}{(1 - \eta)^2} - 12\, \frac{\eta}{1 - \eta}\, \tilde{K} z^{\mu - 1}\right]^2. \tag{26}$$

In this expression, the competition between the two limits $z \to \infty$ and $J \to \infty$ clearly appears. If $\mu < 1$, the depth of the potential goes to infinity too slowly, and we get nothing but pure hard spheres:

$$\chi^{-1} = \frac{(1 + 2\eta)^2}{(1 - \eta)^4}. \tag{27}$$

In the language that we are using, only Region I is present. On the other hand, if $\mu > 1$, the depth of the well increases too rapidly, and a nonphysical behaviour is obtained, namely

$$\chi^{-1} = \left(\frac{12\eta}{1 - \eta}\right)^2 \tilde{K}^2 z^{2(\mu - 1)}. \tag{28}$$

Now, Region II fills the $\eta - \tilde{K}$ plane.

However, for the particular value $\mu = 1$, both limits balance and one gets a physically meaningful result different from hard spheres, namely,

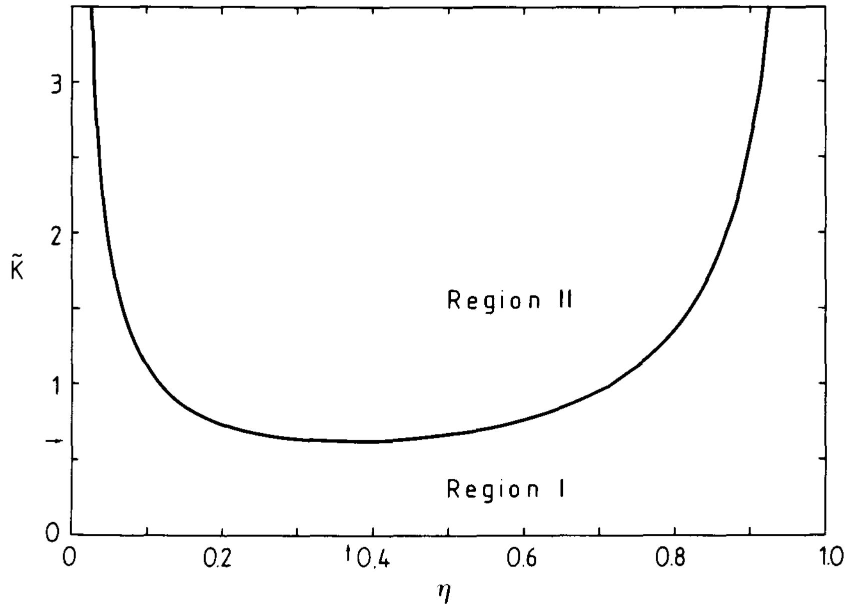
$$\chi^{-1} = \left[\frac{1 + 2\eta}{(1 - \eta)^2} - 12\, \frac{\eta}{1 - \eta}\, \tilde{K}\right]^2. \tag{29}$$

Therefore, in the context of the MSA, it seems legitimate to identify the adhesive-hard-sphere limit of the HCY potential (5) as the limit $z \to \infty$, $J \to \infty$, taken with $J/z = \text{const}$. All the other cases analysed are either nonphysical (divergent equation of state) or trivial (hard spheres). The situation is summarized in the table.

## 3. Results and discussion

The spinodal line obtained from (29) is

$$\tilde{K} = \frac{1}{12}\, \frac{1 + 2\eta}{\eta(1 - \eta)}. \tag{30}$$




Spinodal line in the plane of inverse temperature vs density for adhesive hard spheres in the mean spherical approximation. The arrows indicate the coordinates ($\eta_c$, $\tilde{K}_c$) of the critical point.

This line is plotted in the figure. The minimum of the curve defines the critical point, and its coordinates are

$$\eta_c = \frac{\sqrt{3} - 1}{2} \simeq 0{\cdot}366, \tag{31}$$

$$\tilde{K}_c = \frac{\sqrt{3} + 2}{6} \simeq 0{\cdot}622. \tag{32}$$

The behaviour in the critical region is obtained by expanding (29) around these values. The results are

$$\chi^{-1} = \frac{(6\tilde{K}_c + 1)^8}{3^6} (\eta - \eta_c)^4, \quad \tilde{K} = \tilde{K}_c, \quad \eta \rightarrow \eta_c, \tag{33}$$

$$\chi^{-1} = \left(\frac{12\eta_c}{1 - \eta_c}\right)^2 (\tilde{K} - \tilde{K}_c)^2, \quad \eta = \eta_c, \tag{34}$$

which imply $\delta = 5$ and $\gamma = 2$, respectively. So, the spherical model values of the critical exponents are obtained. In other words, the AHS limit has not played any singular role concerning the critical region.

We can then conclude that the MSA and the PY approximation have a quite different critical behaviour for the AHS limit. We also want to stress the difference in the definition of the AHS limit in both cases. In the PY approximation, the area of the well decreases as $d \ln |d|$ when the width $d$ goes to zero, while in the MSA the area remains finite. Nevertheless, both definitions lead to

$$c(r) \sim d^{-1}, \quad \sigma < r < \sigma + d, \tag{35}$$

when used in the corresponding approximations. Thus, it appears sensible to think that the behaviour of $c(r)$ for $r < \sigma$ plays an essential role in the differences showed by the MSA and the PY approximation near the critical point.

We want to mention that the opposite limit of an infinitely weak and long-ranged attractive tail ($z \to 0$, $J \to 0$, $J/z^2 = \text{const}$) can be analysed in a similar way [10]. This limit has a singular nature and one obtains fully classical values for the critical exponents instead of the spherical model ones.

This work has been supported in part by the Comisión Asesora de Investigación Científica y Técnica of Spain, under grant 1359/82.

## References

[1] Cummings, P. T., and Monson, P. A., 1985, *J. chem. Phys.*, **82**, 4303.
[2] Baxter, R. J., 1968, *J. chem. Phys.*, **49**, 2770.
[3] Fishman, S., and Fisher, M. E., 1981, *Physica* A, **108**, 1.
[4] Waisman, E., 1973, *Molec. Phys.*, **25**, 45.
[5] Cummings, P. T., and Stell, G., 1983, *J. chem. Phys.*, **78**, 1917. Notice a misprint in the equation (A 9): the factor $e^z$ should be omitted.
[6] See figure 7 of [1].
[7] See, for instance, Sengers, J. V., and Levelt Sengers, J. M. H., 1978, *Progress in Liquid Physics*, edited by C. A. Croxton (Wiley), p. 103.
[8] Parola, A., and Reatto, L., 1984, *Physica* A, **125**, 255.
[9] Gallerani, F., Lo, Vecchio, G., and Reatto, L., 1985, *Phys. Rev.* A, **31**, 511; **32**, 2526.
[10] Høye, J. S., Stell, G., and Waisman, E., 1976, *Molec. Phys.*, **32**, 209.