Nonexistence of Solidlike Solutions to the Mean-Spherical-Model Equations*

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(Received 22 June 1972)

We consider the mean-spherical-model (MSM) equation for systems composed of radially symmetric particles. It is shown that for all densities less than close packing no physically satisfactory solidlike (i.e., nonradial) solutions exist to the MSM equation. The Percus–Yevick equation for hard-core particles (i.e., hard disks in two dimensions and hard spheres in three dimensions) is a special case of the MSM equation.

From the work of Alder and Wainwright it is known that a fluid-solid phase transition occurs in systems composed of hard disks (in two dimensions) and hard spheres (in three dimensions). More recently, it has become known that the fluid-solid transition in hard-core systems is intimately related to the fluid-solid transition in real atomic systems.

The fluid phase solution of the Percus–Yevick equation is quite accurate when describing the fluid phase. Thus, one might hope that solidlike solutions to the PY equation might also exist and provide a description of the fluid-solid transition in hard-core systems. Indeed, Percus has speculated that nonradial solutions might occur at high enough densities. However, the purpose of this Letter is to prove that at densities less than close packing there are no physically satisfactory solidlike (i.e., nonradial) solutions for the PY equations for hard spheres or hard disks. More generally, we prove the nonexistence of solidlike solutions to the mean-spherical-model (MSM) equations for which the hard-core PY equations are special cases.

The MSM equation is the Ornstein-Zernike equation

\[ h(\vec{r}) = c(\vec{r}) + \rho \int d\vec{r}' c(\vec{r}' \cdot \hat{r} - \vec{r}) \]  \hspace{1cm} (1)

plus the closure relations

\[ h(\vec{r}) = -1, \quad |\vec{r}| < \sigma, \quad c(\vec{r}) = \nu(|\vec{r}|), \quad |\vec{r}| > \sigma. \]  \hspace{1cm} (2)

Here, \( h(\vec{r}) = g(\vec{r}) - 1 \), where \( g(\vec{r}) \) is the usual pair distribution function; \( \rho \) is the particle density; and \( c(\vec{r}) \) is the direct correlation function. With \( \nu(|\vec{r}|) \) and \( \sigma \) provided as known quantities, Eqs. (1) and (2) can be solved for the unknowns: \( c(\vec{r}) \) for \( |\vec{r}| < \sigma \) and \( h(\vec{r}) \) for \( |\vec{r}| > \sigma \). When \( \nu(|\vec{r}|) = 0 \), the MSM equation is the PY equation. The closure relations given in Eq. (2) are appropriate for systems composed of radially symmetric particles.

In Fourier-transform space, the Ornstein-Zernike equation is the algebraic relation

\[ -\rho \hat{h}(\vec{k}) = \rho(\vec{k})[1 + \rho(\vec{k})]^{-1}. \]  \hspace{1cm}

Here, \( \rho(\vec{k}) = -\rho \hat{c}(\vec{k}) \); \( \hat{c}(\vec{k}) \) is the Fourier transform of \( c(\vec{r}) \), that is, \( \hat{c}(\vec{k}) = \int d\vec{r} c(\vec{r}) \times e^{-i\vec{r}\cdot\vec{k}} \); and \( \hat{h}(\vec{k}) \) is the Fourier transform of \( h(\vec{r}) \).

A fluid solution to the MSM equation is one in which \( c(\vec{r}) = c(|\vec{r}|) \) [and as a result, \( g(\vec{r}) = g(|\vec{r}|) \)]. For a solidlike solution \( c(\vec{r}) \) and \( g(\vec{r}) \) depend on the direction of \( \vec{r} \) as well as its magnitude.

When considering the possibility of an angular-dependent solution, we make explicit use of the following conditions:

(i) \( \nu(|\vec{r}|) \) is integrable;
(ii) \( h(\vec{r}) \) is finite and piecewise continuous;

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(iii) $1 + p_0(k) = 1 + p^*(k) > 0$; i.e., the structure factor, $1 + p^*(k)$, is real, positive, and finite;
(iv) $p(0)$ is finite; i.e., the compressibility is greater than zero.

Condition (i) is simply a statement on the class of models considered herein. The assumption of a finite structure factor in (iii) (which is a sufficient but not necessary condition for the proof) and conditions (ii) and (iv) are physically reasonable for densities less than close packing. The positivity and realness of the structure factor are rigorous conditions on all stable systems.

Straightforward functional differentiation proves that the solution of the MSM equation is equivalent to solving the following variational problem:

$$
\frac{\partial I}{\partial c(\bar{\tau})} = 0, \quad |\bar{\tau}| < \sigma,
$$

where, for a system of dimension $d$,

$$
I = p(0) + (2\pi)^{d-1} \int d\vec{k} \{ p(\vec{k}) - \ln[1 + p(\vec{k})] \}.
$$

The existence of the functional $I$ is proved from conditions (i), (ii), and (iv).\(^7\)

In two dimensions, $d = 2$, an angular-dependent solution can be expressed as $c(r, \theta)$, where $r = |\bar{\tau}|$

$$
I_\beta = -p_0(0) + (2\pi)^{-1} \int_0^{2\pi} k \, dk \int_0^{2\pi} d\theta \{ p_0(k) + \beta p_1(k, \theta_k) - \ln[1 + p_0(k) + \beta p_1(k, \theta_k)] \}.
$$

If an angular-dependent solution to Eq. (3) exists, and if it is given by $c = c_0 + c_1$, then $\partial I_\beta / \partial \beta = 0$ for $\beta = 1$. However, if for all nonzero $c_1$, $\partial I_\beta / \partial \beta = 0$ for $\beta = 0$ only, then radial solutions are the only possible solutions to the MSM equation. We show below that, indeed, $\partial I_\beta / \partial \beta = 0$ for $\beta = 0$ only.

From Eq. (11) and Eq. (9) it is found\(^8\) that

$$
\partial I_\beta / \partial \beta = (2\pi)^{-1} \int_0^{2\pi} k \, dk \int_0^{2\pi} d\theta \{ p_0(k) + \beta p_1(k, \theta_k) \}/[1 + p_0(k) + \beta p_1(k, \theta_k)],
$$

and

$$
\partial^2 I_\beta / \partial \beta^2 = (2\pi)^{-1} \int_0^{2\pi} k \, dk \int_0^{2\pi} d\theta \{ p_0(k, \theta_k) \}/[1 + p_0(k) + \beta p_1(k, \theta_k)]^2.
$$

Equations (12a), (12b), and (9) imply $\partial I_\beta / \partial \beta = 0$ for $\beta = 0$, and $\partial^2 I_\beta / \partial \beta^2 > 0$ for $0 < \beta < 1$. Further, conditions (ii) and (iii) imply that both of these derivatives are nonsingular for $0 < \beta < 1$. As a result,

$$
\partial I_\beta / \partial \beta = 0 \text{ for } \beta = 0 \text{ only}.
$$

Thus, nonradial solutions to the MSM equation do not exist in two dimensions.

For three dimensions, the proof carries through also. The only changes are essentially notational. Within factors of $2\pi$, the $r$ and $k$ integrations are changed from $\int_0^r r \, dr$ and $\int_0^r k \, dk$ to $\int_0^{2\pi} r \, dr$ and $\int_0^{2\pi} k^2 \, dk$, respectively. The polar angle $\theta$ is replaced by $\varphi$, and the $(2\pi)^{-1} \int_0^{2\pi} d\theta$ integration becomes $(4\pi)^{-1} \int_0^{\pi} d\varphi \sin \varphi$.

In summary, we have shown that angular-dependent solutions to the MSM equations do not exist for systems composed of radially symmetric particles. Thus, the PY equations for hard disks and hard spheres will not predict the solid phases that are observed in such systems. Further, the direct correlation function $c(\bar{\tau})$, for a solid composed of radially symmetric particles, must depend on the orientation of $\bar{\tau}$ (as well as its magnitude) for $|\bar{\tau}| > \sigma$.

*Work supported by the National Science Foundation and the donors of the Petroleum Research Fund as ad-
ministered by the American Chemical Society.

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\footnote{F. Lado, J. Chem. Phys. 49, 3092 (1968).}


\footnote{J. K. Percus, in Equilibrium Theory of Classical Fluids, edited by H. L. Frisch and J. L. Lebowitz (Benjamin, New York, 1964), Sect. 10.}

\footnote{H. C. Andersen and D. Chandler, to be published.}

\footnote{Making use of the inequalities \( x(1 + x)^{-1} \leq \ln(1 + x) \leq x \) for \( x > -1 \), one shows that \( -\rho(0) \leq I \leq \rho(0) - 1 - c(0) \). Condition (iv) says that \( \rho(0) \) is finite, and conditions (i), (ii), and (iv) can be applied to prove that \( -[1 + c(0)] \) is bounded and positive.}

\footnote{Equations (12a) and (12b) are derived by commuting the \( \beta \) differentiation with the integrations. This procedure is legitimate since conditions (ii) and (iii) imply that the integrals in Eqs. (12a) and (12b) are nonsingular for \( 0 \leq \beta \leq 1 \).}