THE SOLID SPHERE MODEL IN STUDIES OF CRYSTAL STABILITY

E. A. Arinshtein and Ya. B. Gorelik

The possibility of employing the hard sphere model in studies of real, stable, inert-gas crystals is considered. On the basis of the firmly established phase transition criterion for a model system the stability curve of a real crystal is found, with attractive forces considered by first-order perturbation theory. The result obtained is compared with experiment.

As has been demonstrated in [1-4], the crystalline state and the crystal—liquid phase transition may be explained by purely repulsive interactions, with attractive forces in this case playing only the role of perturbations. The simplest model of a system with purely repulsive forces is the solid sphere model with potential

$$\varphi (r) = \begin{cases} \infty & r < d \\ 0 & r > d, \end{cases}$$

where d is the sphere diameter. In such a system the existence of a phase transition corresponding to the crystal—liquid phase transition [5] has been firmly established, with the transition criterion

$$v = 1.59 v_0,$$

where v is the specific volume of the system and v_0 is the volume assignable to a single particle in the density packed lattice,

$$v_0 = d^3/\sqrt{2}.$$  \hspace{1cm} (3)

We wish to employ these two factors — the relatively simple model and the existence of a strict phase transition criterion — in a study of real crystal stability, while considering attractive forces by perturbation theory according to [6]. We shall use a variation of the Bogolyubov principle [7], which establishes a method for best selection of model system parameters in terms of real interaction with the aid of the variation equation

$$\frac{3}{8d_0} (F_0 + \langle u - u_0 \rangle_0) = 0.$$  \hspace{1cm} (4)

Here F_0 is the free energy of the model system, u is the real potential energy; \langle \cdot \rangle_0 indicates averaging over the model system.

If the real interaction is described by a Lennard−Jones potential

$$u (r) = 4\varepsilon \left( \left( \frac{z}{r} \right)^{12} - \left( \frac{z}{r} \right)^6 \right),$$  \hspace{1cm} (5)

then for our purposes, instead of u we choose the first term of Eq. (5), describing the repulsive force \(u_{\text{rep}}\). For a system of solid spheres the volume \(v_0\) may be chosen as the single variation parameter of Eq. (4).

Moreover, considering that the expression for free energy of the model system can be represented as a
function of the ratio \( v_0/v \), then for the first term of Eq. (4) we obtain

\[
- \theta \frac{\partial}{\partial v_0} \ln \frac{Q(v_0,v)}{N} = - \frac{\theta}{v_0} \frac{\partial}{\partial v_0} \ln \frac{Q(v_0,v)}{v_0} \cdot \frac{v_0}{v} \cdot \frac{\partial}{\partial v_0} \ln \frac{Q(v_0,v)}{N},
\]

(6)

On the other hand,

\[
P = \theta \frac{\partial}{\partial v} \ln \frac{Q(v_0,v)}{N} = - \frac{\theta v_0}{v^2} \frac{\partial}{\partial v_0} \ln \frac{Q(v_0,v)}{v_0},
\]

(7)

whence we obtain

\[
\frac{\partial}{\partial v_0} \left( - \theta \ln Q \frac{v_0}{N} \right) = \frac{v}{v_0} P,
\]

(8)

where \( Q \) is the canonical statistical sum of the system of hard spheres, \( N \) is the number of particles, and \( P \) the corresponding pressure.

To calculate the second term of Eq. (4) we use the Ornstein method for derivation of the van der Waals equation, described in [8]. (We note that for more accurate calculation it is necessary to use the results of computer calculation of the binary distribution function of the solid sphere system [5].) Then, considering that here

\[
\langle u_0 \rangle_0 = 0
\]

(9)

and calculating the integral \( \langle u_{\text{rep}} \rangle_0 \), we have

\[
\langle u_{\text{rep}} \rangle_0 = \gamma_1 \frac{\mu_0^{12}}{(v - v_0)^2 v_0^6},
\]

(10)

which, considering Eq. (2), at the transition point gives

\[
\frac{\partial}{\partial v_0} \langle u_{\text{rep}} \rangle_0 = \gamma_2 \frac{\mu_0^{12}}{v_0^6} \left|_{v = v_0} \right. ,
\]

(11)

where \( \gamma_1 \) and \( \gamma_2 \) are numerical constants.

As was demonstrated in [5], the expression for the pressure of a system of solid spheres on both
sides of the transition point may be written in the Padé form

\[
P = \frac{\theta}{v} \left( 1 + \frac{v_0/v + 0.063 (v_0/v)^2 + 0.017 (v_0/v)^3}{1 - 0.561 (v_0/v) + 0.081 (v_0/v)^2} \right).
\]

(12)

Considering Eqs. (2), (8), we now obtain an expression for \( v_0 \)

\[
-\theta + \gamma_2 \frac{1}{v_0^6} = 0.
\]

(13)

Solving for \( v_0 \) and substituting in Eq. (12), with consideration of Eq. (2), we obtain for the repulsive por-
tion of the potential at the transition point

\[
P_0 = \gamma_1 \frac{\mu_0^2}{v_0^6} \left( \frac{\theta}{v} \right)^{\gamma_4}, \quad \gamma_4 > 0.
\]

(14)

To consider the influence of attractive forces on the transition curve we use the perturbation theory de-
volved in [6]. The perturbation theory series may be written in the following form:

\[
F = F_0 - \theta \ln \left( \sum \left[ f_{\text{at}}(ij) \right] \right),
\]

(15)

where \( F_0 \) is the free energy of the model system with parameters defined by Eq. (13) and \( f_{\text{at}} \) is the binary attractive force function.