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Properties of a bound ensemble of repelling atoms

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Various data are combined to analyze the behavior of condensed rare gases at high pressures or systems of repelling atoms interacting via a pair interaction. An analysis based on numbers of nearest neighbors of a test atom shows that the crystalline state is not the most stable thermodynamically for a system of repelling atoms at high pressures. Rather, the equilibrium solid state of this system at nonzero temperature is an irregular mixture of small domains/clusters of fairly rigid, close-packed structures. This means that an ensemble of repelling atoms has a polycrystalline structure at high pressures and low temperatures. Parameters of this system at low temperatures and its melting curve are considered from different standpoints.

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INTRODUCTION

We consider a bulk ensemble of atoms with a repulsive pair interaction. Rare gases at high pressures are an example of such a system. Therefore, on one hand, the behavior of such atomic systems may be understood from the analysis of rare gases at high pressure, and on the other hand, the study of ensembles of strongly repelling atoms gives additional information about highly compressed rare gases and other materials. We now link the information about rare gases at high pressures and about properties of ensembles of repelling atomic particles in order to construct a general picture of the behavior of such systems.

Our goal here is to develop the properties of ensembles of repelling atomic particles, including rare gases at high pressures, through the use of relatively simple models of such systems. We begin by introducing the number q of nearest neighbors of a test internal atom. For crystals with close-packed structures, i.e., fcc or hcp structures, this number is, of course, 12. Comparisons of structures on the basis of the number of nearest neighbors allows us to draw conclusions about various properties of a system of strongly repelling atoms. First, we find that, at thermodynamic equilibrium at low but nonzero temperatures, atoms of this system do not form a crystal lattice of close-packed structure. Second, we find some insights into a general statement by Stishov[1] that, under some conditions, the melting curve on the pressure-temperature phase diagram of this system does not terminate at a critical point, but continues up to high temperatures and pressures. Our conclusions suggest that there may be cases with something resembling a critical point, and other cases with no such point. Nevertheless, at high pressures, the states separated by the traditional solid-liquid coexistence curve are not the crystal and liquid states, as they are at low pressures. Rather, both states of this phase transition correspond to disordered distributions of atomic particles and are states of dense packing structure and loose packing structure.[2]

PAIR INTERACTION OF RARE GAS ATOMS

At pressures satisfying the criterion

$$p \gg p_o = \frac{D}{R_e^3}, \tag{1}$$

interatomic repulsion is the dominant internal force determining the system's phase equilibrium. Then, only the interactions between nearest neighbors are of importance, and the pair interaction potential can be approximated by

$$U(R) = U(R_o)\left(\frac{R_o}{R}\right)^\gamma = \frac{A}{R^\gamma}, \quad \gamma \gg 1. \tag{2}$$

In this work, specific values of the parameters D, the depth of the two-body potential well, and R_e, the equilibrium distance for two bound atoms, are taken from literature sources[3–6] and are collected in Table I.

In considering a system of interacting rare gas atoms, we assume the interatomic interactions can be treated strictly as pair interactions, and that three-body and higher interactions are not significant. The predominant cause of repulsion between two atoms is the overlapping of wave functions of their valence electrons and is created mostly in a coordinate region close to the axis that joins the atoms. Hence, interaction of a test atom with each of its neighboring atoms is essentially independent of other atom-atom interactions. (We thereby neglect regions in which wave functions of three or more atoms overlap.)

Next, the potential energy of interaction between two atoms is small compared to any configurational or electronic excitation energy of the system. This condition is met at low to moderate pressures. At extremely high pressures that make interatomic distances sufficiently small, the valence elec-

TABLE I. Parameters of the pair interaction potential for rare gas atoms and the reduced parameters of systems consisting of interacting atoms of rare gases, for the interaction potential γ, R_o (Ref. 7) if $U(R_o)=0.3$ eV.

	Ne	Ar	Kr	Xe
R_e (Å)	3.09	3.76	4.01	4.36
D (K)	42	143	200	278
m (a.m.u.)	20.18	39.95	83.80	131.3
$p_o=D/R_e^3$ (MPa)	20.2	37.1	43.0	47.1
γ	7.6	8.1	7.7	5.9
R_o [Å]	2.07	2.85	2.99	3.18

trons' wave functions may change enough to induce a transition from an insulating state to a metallic state. Here, we consider pressures below that of metallization. In particular, xenon metallization is expected at pressures of about 150 GPa;[8–10] for other rare gases this transition proceeds at higher pressures. The pressure range we consider here lies below this limit.

A SYSTEM OF HARD SPHERES

According to the data in Table I, $\gamma \gg 1$ for the pair interaction potential (2) of rare gas atoms. This allows us to describe an ensemble of repelling atoms with an almost-hard-sphere model, and hence to draw on a hard-sphere model to analyze the behavior of an ensemble of repelling atoms at low temperatures and high pressures. For this analysis, we draw on simple experiments with hard balls,[11–13] and simulations with hard spheres.[14,15] The discussion will then relate the results of this simple model to the behavior of the compressed, solid rare gases, as found in experiments and simulations.

It is convenient to characterize the distribution of spheres in a space by the packing density,[2] given by

$$\varphi = \frac{4\pi}{3} r^3 N, \tag{3}$$

where r is the sphere's radius, N is the number density of spherical particles, and the packing density φ is the fraction of the space occupied by the balls. The maximum value of this parameter for hard spheres corresponds to a close-packed crystal lattice. For such crystals of fcc or hcp structure, the packing density is

$$\varphi_{cr} = \frac{\pi\sqrt{2}}{6} = 0.74. \tag{4}$$

The packing density φ of an ensemble of hard balls was initially found from experiments based on filling a container with hard balls. The observed value is $\varphi_d = 0.64$.[12] A more precise value for the packing density of this system was obtained from computer simulations and is[14]

$$\varphi_d = 0.644 \pm 0.005. \tag{5}$$

These results coincide within the limits of their accuracy and lead to the conclusion that an ensemble of hard spheres does not form a crystal lattice. We analyze this result within the framework of a mean-field approach for a system of atoms with a steep repulsive interatomic potential. It is convenient to characterize the state of this system by the mean coordination number q, which is the average number of nearest neighbors of an internal test atom. Clearly, in the limit $\gamma \to \infty$, i.e., for the system of hard balls, this value is connected with the packing density φ. Indeed, using the formula[16]

$$q = 12 \frac{\rho_{cr}}{\rho}, \tag{6}$$

where ρ_{cr} is the crystal density and ρ is the density of the state of interest. Equation (4) gives us

$$q = 12 \frac{\varphi}{\varphi_{cr}} = 16.2\varphi, \tag{7}$$

where φ_{cr} and φ are, respectively, the packing densities of the crystal state and the state under consideration. We take that of the crystal state to be $\varphi_{cr} = \pi\sqrt{2}/6 = 0.7405$.

From this relation and from formula (5) for dense random packing, we have $q = 10.4 \pm 0.1$ for that state. This is close to the coordination number of liquid rare gases at low pressures, in which atoms are bonded by the attractive forces between them, with $q = 10.1 \pm 0.1$.[16,17] Therefore, their structure suggests that compressed rare gases are, in some sense, more like liquid rare gases at low pressures than like low-pressure solids. In any case, from this it follows that compressed rare gases cannot have a crystalline structure at low temperatures.

Note that this comparison refers to a phase transition within the conventional part of the melting curve $(p \ll p_o)$, from the crystalline state $(q = 12)$ to the liquid state.

THE VIRIAL THEOREM AND THE EQUATION OF STATE FOR AN ENSEMBLE OF REPELLING ATOMS

Clearly, the previous results imply that the solid states of rare gases under pressure are not regular, crystalline solids, or even disordered but close-packed arrays. The reported structures, as discussed below, must have some irregularities in the form of void spaces that lower their densities from that of close-packed systems. Here we show that the crystalline aggregate state of the system of repelling atoms is not the most stable thermodynamically, relative to a disordered aggregation of clusters with some void space. We will base the results on the virial theorem for a system of repelling atoms with pair interactions.

We represent the equation of state for atoms interacting through the potential (2) by invoking the virial theorem, yielding the form[18,19]

$$T = pV - \frac{\gamma}{3}\overline{U}, \tag{8}$$

where V is the volume per atom, and $\overline{U}$ is the average interaction potential per atom. We have, in the mean-field approximation,

$$V = \frac{a^3}{\sqrt{2}} \frac{12}{q}, \quad \overline{U} = \frac{q}{2} U(a), \tag{9}$$

where a is the distance between nearest neighbors, and the pair interaction potential $U(a)$ is given by formula (2). In the limiting case (1), we have $pV \gg T$; i.e., Eq. (9) allows one to estimate the pressure from just its second term, as

$$p = 2\sqrt{2}\gamma \left(\frac{q}{12} \right)^2 \frac{U(a)}{a^3}. \tag{10}$$

We demonstrate below the validity of this formula in the case of a close-packed crystal lattice. Let us draw a plane parallel to a symmetry plane of this lattice, so that the pressure is the force per unit area between atoms located on different sides of the crossing plane. The pressure is thus

$$p = \frac{mf_x}{s} = \frac{mf\cos\theta}{s}, \tag{11}$$

where m is the number of nearest neighbors of a test surface atom which are above and below the separation plane, s is the surface area per atom, and f_x is the force projection onto the perpendicular to the separation plane. Hence this force acts between a test atom and its nearest neighbor outside the separation plane; f is this force, and θ is the angle between the line connecting interacting atoms and the perpendicular to the separation plane. From this, we have for the $\{100\}$ separation plane, with $m=4$, $s=a^2$, $\cos\theta=1/\sqrt{2}$,

$$p = \frac{4f(a)}{\sqrt{2}a^2} = \frac{2\sqrt{2}}{a^2}\left|\frac{dU(a)}{da}\right| = \frac{2\sqrt{2}}{a^3}\gamma U(a). \tag{12}$$

In the case of the $\{111\}$ direction of the separation plane, we have $m=3$, $s=\sqrt{3}a^2/2$, $\cos\theta=\sqrt{2/3}$, so that

$$p = \frac{3f(a)}{(\sqrt{3}/2)a^2}\sqrt{\frac{2}{3}} = \frac{2\sqrt{2}}{a^2}\left|\frac{dU(a)}{da}\right| = \frac{2\sqrt{2}}{a^3}\gamma U(a). \tag{13}$$

As we see, formulas (12) and (13) are transformed into formula (10) in the case $q=12$.

These formulas allow us to compare the crystalline state of the repelling atoms with a random distribution of the same atoms characterized by a mean coordination number q. We analyze the possibility of a phase transition between these states when the total number of repelling atoms, the pressure, and the temperature are conserved. The condition for equilibrium of the two phases[20] is the equality of the Helmholtz free energies of two phases, $\Delta F=\Delta E-T\Delta S=0$, and ΔE and ΔS are the differences of the internal energies and entropies of the two phases, respectively. (Strictly, at constant pressure, one should use the Gibbs free energy difference, $\Delta G=\Delta H-T\Delta S$, but the difference can be neglected here.) In order to ascertain the stability of the crystalline state of the system repelling atoms, we take into account that the transition from the crystal to a disordered state corresponds to an increase of the entropy. Because $p=\text{const}$, we have

$$\Delta E = n(\Delta\overline{U} + p\Delta v), \tag{14}$$

where $\overline{U}$ is the average interaction energy per atom and v is the volume per atom. From formula (9), it follows for the transition from the crystalline state with $q=12$ to another state characterized by a coordination number q that

$$\begin{aligned}\frac{\Delta E}{n} &= \left(1+\frac{\gamma}{3}\right)(\overline{U}_{cr}-\overline{U}_r) = \left(1+\frac{\gamma}{3}\right)\left[6U(a_{cr}) - \frac{q}{2}U(a_r)\right]\\ &= 6U(a_{cr})\left(1+\frac{\gamma}{3}\right)\left[1-\frac{q}{12}\frac{U(a_r)}{U(a_{cr})}\right],\end{aligned} \tag{15a}$$

where $U(a)$ is the pair interaction potential (2) at the distance a between interacting atoms, and a_{cr} and a_r are, respectively, the (mean) distances between nearest neighbors in the crystalline state and in the state with randomly distributed atoms. (Here we do not attempt to quantify the degree of randomness or to optimize q, but merely distinguish that state from the high-density crystal.) In the mean-field approach, the average interaction potential per atom is $\overline{U}_{cr}=6U(a_{cr})$ and $\overline{U}_r=qU(a_r)/2$. The condition $p(a_{cr})=p(a_r)$ gives

$$\frac{\Delta E}{n} = 6U(a_{cr})\left(1+\frac{\gamma}{3}\right)\left[1-\left(\frac{12}{q}\right)^{(\gamma-3)/(\gamma+3)}\right]. \tag{15b}$$

Only the final factor is negative, so that a transition from the crystalline state to any random state of the system of repulsing atoms with a lower density or an increase in the mean distance of nearest neighbors corresponds to energetic stabilization, i.e., to $\Delta E<0$. Clearly, as long as $T>0$, $\Delta S>0$ for any transition from the crystalline (ordered) state of atoms to any disordered (random) state. (We introduce the temperature constraint to avoid any issues of the third law of thermodynamics.) Hence, the crystalline state of a system of atoms with a steeply varying repulsive interaction potential $(\gamma>3)$ is not stable thermodynamically with respect to a state with a random distribution of atoms. Hence, the crystalline state of such a system is not realized under conditions of thermodynamical equilibrium, so long as the random state has any local stability under the same conditions. In the present case, that stability is due to the externally applied pressure.

Generalizing, we use the analogy of formula (15) to find the change of the internal energy of the system ΔE between states with coordination numbers q_1 and q_2:

$$\frac{\Delta E(q_1\to q_2)}{n} = \frac{q_1}{2}U(a_1)\left(1+\frac{\gamma}{3}\right)\left[1-\left(\frac{q_1}{q_2}\right)^{(\gamma-3)/(\gamma+3)}\right]. \tag{16}$$

This gives $\Delta E(q_1\to q_2)<0$ if $q_1>q_2$, a natural consequence of relieving the repulsive force. For this transition, the entropy change ΔS per atom can have either sign. If the transition is accompanied by a volume decrease, then it must also exhibit an entropy decrease if the transition takes place between two disordered states with random distributions of atoms. Hence, in principle, a phase transition is possible between random states. Note that in the limit $\gamma\to\infty$, formula (16) gives $\Delta E/n=p\Delta V$, where ΔV is the volume change per atom. In this limit, we have $p\Delta V=T\Delta S$, where ΔS is the entropy change per atom, and if this phase transition corresponds to a decrease of the coordination number q, this implies an increase of the specific volume V and a decrease of the specific entropy S.

Thus, from the virial theorem, it follows that the crystalline system of repelling atoms is unstable with respect to a decrease of the mean coordination number. A nonregular distribution of atoms is characterized by a lower interatomic repulsive energy, and because the entropy of a nonregular atomic distribution is higher than that of a crystal lattice, we conclude that the ordered state of this system is unfavorable thermodynamically. This analysis does not allow us to find the optimal mean coordination number of an atomic distribution, because we cannot determine the entropies of distributions with a given coordination number. Nonetheless, it demonstrates the thermodynamic instability of the crystalline state of an ensemble of repelling atoms.

While our mean-field model shows the thermodynamic instability of the uniform lattice distribution for repelling atoms, this does not prohibit stability of a polycrystalline structure, consisting of small-domain clusters, so long as the density of such a system is lower than that of the uniform crystal. In this case the system is nonuniform, so that the virial theorem is not applicable. Thus, on the basis of the virial theorem one can state only that the uniform crystal state of the system of strongly repelling atoms is unstable thermodynamically, but this result does not determine the optimal atomic distribution in this case.

PHASE TRANSITION IN AN ENSEMBLE OF REPELLING ATOMS

The system of repelling atoms admits a phase transition. This is demonstrated by both computer simulations and experiments. This is all consistent with Stishov's statement[1] that the melting curve has no critical point as experimental temperatures are increased. Here we analyze the results of computer simulations and experimental results[21–29] for compressed rare gases.

According to computer simulations of a hard-sphere system,[14,15] the melting corresponds to a transition between states of the following values of the packing density

$$\varphi_{dr} = 0.545, \quad \varphi_{lr} = 0.494. \tag{17}$$

Because the state of higher density has a density too low to be the crystalline state, this is not a traditional solid-liquid phase transition. Following Ref. 2, we call the states associated with this transition the dense random and loose random states. Without inquiring into the diffusive or compliant properties of the loose random state, we shall refer here to the coexistence curve for this transition as the "melting curve." On the basis of formula (7), we have $q_{dr}=8.8$ for the number of nearest neighbors of a test atom in the dense random packing state at the melting curve, and $q_{lr}=8.0$ for the loose random packing state, with $\varphi=0.494$. These results correspond to the limiting case $\gamma\to\infty$ for the pair interaction potential (1).

Accepting the hypothesis of a polycrystalline structure of rare gases at high pressure, one can use this simple model: the atoms are located in identical balls of radius r, and in these balls the atomic number density is the same as in a close-packed crystal. In accordance with formulas (4) and (7), the average packing densities for the solid and liquid states of the balls are, respectively,

$$\varphi_{sol} = 0.55, \quad \varphi_{liq} = 0.46, \tag{18}$$

that more or less correspond to formulas (17). Note that the atomic densities and packing densities given by formulas (18) do not depend on the ball radius. This means that change of a ball radius leads to a change of pore sizes, but the relation between volumes occupied by atoms and pores does not depend on the ball radius. Hence, at this level of analysis, one cannot yet estimate the extent of short-range order.

We now go beyond the hard-sphere model and analyze the character of the phase transition (assuming that it takes place) for a system of repelling atoms with the interaction potential (2). It is convenient to introduce a parameter with the dimension of length, based on the parameters of the interaction potential (2):

TABLE II. The parameters of a phase transition between the solid or dense random packing state (index *dr*) and liquid or loose random packing state (index *lr*) for a system of repelling atoms (on the basis of Ref. 30).

γ	4	6	8	12	∞
$T/(pV_{dr})$	0.011	0.026	0.036	0.053	0.091
$V_{dr}\sqrt{2}/d^3$	0.254	0.641	1.030	1.185	1.359
$V_{lr}\sqrt{2}/d^3$	0.255	0.649	1.060	1.230	1.499
$\Delta V/V_{dr}$	0.005	0.013	0.030	0.038	0.103
$p\Delta V/T$	0.45	0.50	0.63	0.72	1.16
ΔS	0.80	0.75	0.84	0.90	1.16

$$d = \left(\frac{A}{T}\right)^{1/\gamma}, \tag{19}$$

where T is a temperature we use to define a point on the melting curve. Introducing the pressure p and the change of specific volume (the volume per atom) Δv upon melting, the volumes per atom for the dense random packing (solid) and loose random packing (liquid) states v_{dr} and v_{lr} ($\Delta v=v_{dr}-v_{lr}$), respectively, and the entropy change per atom Δs, we obtain the scaling law for the melting curve[1]

$$p \sim \frac{T}{d^3}, \quad \Delta v \sim v_{dr} \sim v_{lr} \sim d^3, \quad \Delta s \sim 1. \tag{20}$$

Table II gives the parameters on the melting curve for a system of atomic particles with the interaction potential (2) for various γ on the basis of numerical calculations:[30] the equation connecting the the pressure p and temperature T on the melting curve is, of course, the usual equation for coexistence.

From the data of Table II, it follows that the left side of Eq. (8) is small compared with each term of the right-hand side of this equation as we used it. Next, also from Table II, the packing densities on the coexistence curve in the limit $\gamma\to\infty$ coincide with those of formula (17).

Experimental methods of constructing the melting curve for rare gases at high pressures are based on the diamond-anvil cell containing a rare gas compressed by a laser beam. The laser beam heats the rare gas inside the diamond cell through its metal substratum, and is used to measure the rare gas pressure and temperature in the course of its heating. The melting point is found from a change of optical properties of a compressed condensed rare gas. This method allows us to analyze the pressures up to 100 GPa two orders of magnitude higher than those available to classical methods of gas compression (for example, Refs. 21–24 in the argon case).

Even at the highest pressures, the kinetic energy of atoms on the melting curve is small compared to the electronic excitation energy or the ionization potential of these atoms. Hence, thermal excitation and ionization of atoms on the

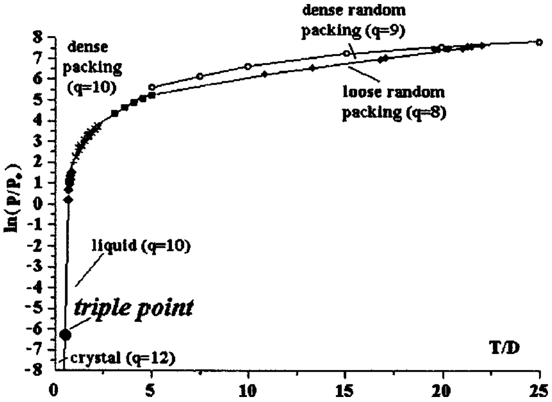

FIG. 1. The melting curve for condensed argon. Experimental data: triangles—Ref. 25, open squares—Ref. 26, closed circles—Ref. 27. A closed square is the triple point, and the full curve is constructed on the basis of these data, and its derivative is given by formula (20). Open circles correspond to evaluations on the basis of the Table II data with using the parameters of the pair interaction potential according to Table I.

melting curve under consideration is negligible and does not influence the phase transitions we consider here. At very high pressures, compression of rare gases creates a strong overlap of the wave functions of the valence electrons that can induce a transition from the van der Waals solid state to the metallic state. This effect is especially strong for xenon, for which the transition to the metallic conductivity is expected at 130–150 GPa.[8–10] In reality, this transition proceeds over a wide pressure range and, evidently, depends on the temperature. This effect can affect the behavior of the melting curve. Moreover, one can expect that the observed decline of the melting curve $T(p)$ for xenon at pressures above 15 GPa and for krypton at pressures above 25 GPa can be attributed to this effect.

In order to avoid concerns regarding metallization effects at high pressures on the behavior of the melting curve, we restrict our discussion to the range of the melting curve of compressed argon shown in Fig. 1. This figure is based on experimental data,[25–27] from which we have constructed the empirical curve based on the relation

$$\frac{dp}{dT} = 4 + a\left[\left(\frac{T}{T_{tr}}\right)^k - 1\right]. \tag{21}$$

In this formula, the derivative dp/dT is measured in MPa/K, and $T_{tr}=83.8$ K is the argon triple point. We take this derivative at T_{tr} to be 4 MPa/K, as follows from the Clausius-Clayperon and Simon equations for argon;[31] the parameters of formula (18) are $a=2.1$, $k=0.78$. One can see that this derivative varies by one order of magnitude (from 4 up to 37 MPa/K) when the temperature along the melting curve varies in the temperature (or pressure) range under consideration, from T_m up to 3400 K.

Let us analyze these experimental results from the standpoint of the above computer simulation. Assuming atoms to interact through pair potential (2) and using the scaling law (19), we obtain $k=3/\gamma$, i.e., the exponent $\gamma \approx 4$ in this case, while according to direct measurements (Table I), the parameter γ is a factor of 2 larger. Next, introducing the parameter d on the basis of formula (18), $U(d)=T$, we obtain at the highest temperature, according to the data of Table I, $d=2.85$ Å. Correspondingly, at this temperature ($T \approx 3400$ K) and pressure ($p \approx 76$ GPa), we obtain the ratio $T/(pd^3)=0.026$, corresponding, according to Table II, to $\gamma=8$; i.e., the exponent of the pair interaction potential (2) at the corresponding interatomic separation for argon (see Table I).

Thus, this analysis shows a partial correspondence between computer simulations of the phase transition for a system of repelling atoms and the experimental data for rare gases if we assume this transition is determined by pair interactions of atoms. The state equation for strongly compressed argon corresponds to computer simulation with the real interaction potential between two argon atoms, while the temperature derivative of the pressure on the melting curve is sharper than that from the argon-argon pair interaction.

At this point we can make some inferences regarding the possible forms that phase diagrams of compressed rare gases may take. Diagrams of this kind of system are shown in Refs. 14, 15, and 28, but the first two of these references do not carry pressures high enough that the free energy of the ordered crystal is higher than that of a disordered form. The third is derived from a molecular dynamics study that finds some body-centered cubic structure, which, because of its lower density, would not be in conflict with the general conclusions found here. We begin by accepting that at low pressures, there is a local minimum, not the absolute minimum, for a disordered solid, and that this minimum is displaced from that of the ordered solid. In Refs. 14 and 15, this is shown as a curve of metastable equilibrium between the disordered solid and a lower-density disordered form, presumably either a liquid or a low-density, very disordered solid, presumably a phase that could be called a glass.

The conclusions reached here show that at high enough pressures, the free energy of the disordered form, quite plausibly the form shown as metastable by Rintoul and Torquato,[14,15] falls below that of the crystalline solid. If this is the case, then the rare gas solids must show a first-order phase transition from crystalline to a dense, disordered solid along a coexistence curve. Furthermore, since there is a coexistence curve of the metastable disordered solid and the lower-density, more disordered form, there may be a point at which the metastable disordered form becomes the more stable solid, the crystalline solid becomes metastable, and both the disordered and crystalline forms can be in equilibrium with the low-density disordered form. In short, this situation would imply a triple point for the crystalline and two disordered forms. An alternative scenario is possible but seems less likely for the rare gas solids as we have discussed them here. This would be the case if the stable disordered form were to branch off continuously from the crystalline form, with a free energy lower than the metastable disordered form. In this case, the transition from crystalline to disordered solid would of course be second-order. These two cases are shown schematically in Fig. 2, as phase diagrams in the space of the variables pressure p and volume fraction ϕ occupied by the particles. The triple point in the first-order case does not appear as such in this representation; in a

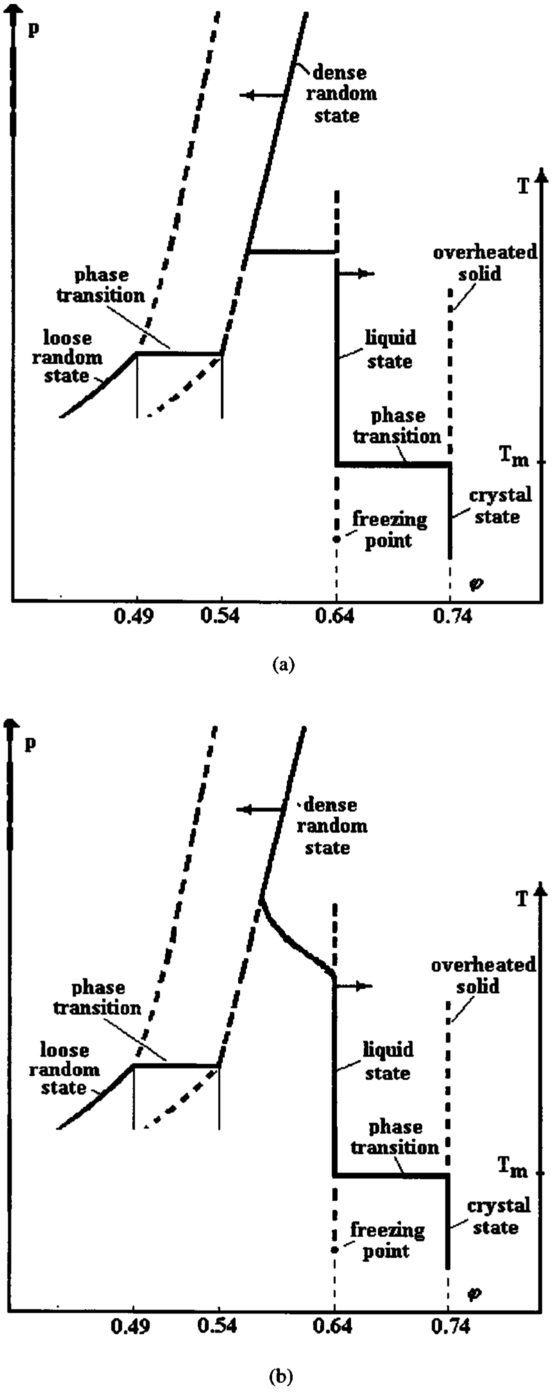

FIG. 2. Schematic phase diagrams for an ensemble of strongly repelling atoms in variables the pressure p and the volume fraction ϕ occupied by the particles, as it was used in Refs. 14 and 15: (a) a first-order transition; (b) a second-order transition. These diagrams are an illustration of data which are given in the text. The dotted curves correspond to metastable states, and the phase transition of first order leads to an increase of the packing parameter ϕ increases from 0.494 to 0.545 for the hard-sphere approach.[14,15] The thermodynamically stable state at high pressures relates to the polycrystal (domain) structure of repelling atoms, and hence the packing parameter has the value $\phi = 0.644$ in the limit of high pressures, but not the value $\phi = 0.7405$ of the crystal that is given in the diagram of Refs. 14 and 15 as the limiting value of the packing parameter.

pressure-temperature diagram, it appears as such, at the point at which Fig. 2(a) shows its dotted horizontal line. Fig. 2(b) is the second-order possibility. Until this study is carried further, constructing plausible p-T phase diagrams as counterparts to Fig. 2 would be highly conjectural.

STRUCTURE OF RARE GAS SYSTEMS AT HIGH PRESSURES

As demonstrated by modeling an ensemble of repelling atoms by hard balls,[2,11–13] and by computer simulation of the system of hard, repelling spheres,[14,15] the system of strongly repelling atoms under pressure does not have a crystalline structure at high pressures and low temperatures. Information is also available from x-ray diffraction investigations of compressed rare gases at low temperatures. If we start from the crystal state of a rare gas and increase the pressure, a stacking instability[27,29,32] occurs at some pressures that leads to a transition from the face-centered lattice to the hexagonal lattice. In particular, for xenon at low temperatures, a stacking disorder starts to appear at a pressure of about 4 GPa ($p \approx 100 p_o$). At pressures above 70 ± 5 GPa ($p \approx 2000 p_o$), high-resolution x-ray diffraction studies show that the basic structure of the system of repulsing atoms is hexagonal close-packed.[29,33] However, such measurements give only one aspect of the atomic structure, namely, that the correlation in positions of nearby atoms corresponds to the hexagonal structure. Simultaneously, a pressure increase reduces the long-range order of the structure, even while nearby atoms remain correlated. This results in the appearance of characteristic scattering peaks for fcc and hcp structures in the high-resolution x-ray diffraction study, but nevertheless the correlation length is comparable with the distance between nearest atoms.

On the basis of such investigations, one can suggest that the system of repelling atoms at high pressures consists of individual domains/solid clusters of fcc and hexagonal structure, or of only one of these structures. There could even be domains with arrangements of layers different from the ABABAB and ABCABC regular patterns of the fcc and hcp lattices. These clusters are presumably oriented randomly, with nearest clusters connected by fixed “bonds.” Voids or vacancies on the boundaries between neighboring clusters lower the average number of nearest neighbors q in comparison with that for the close-packed crystal, for which $q = 12$. At high pressures, the number of nearest neighbors varies from $q = 10.4$ to $q = 8.8$ as we move from low temperatures to the melting curve. These data are not consistent with recent molecular dynamics simulations of xenon at high pressures;[28] for those calculations, a bcc structure was assumed. Since the number of nearest neighbors is precisely $q = 8$ for a body-centered crystal, the assumption of this structure is in disagreement with our results and seems problematic. However, the presence of some bcc regions together with zones with other packing could be compatible with our conclusions. However the observations may be explained alternatively in terms of a locally close-packed structure that is globally disordered.

The experiments certainly imply local hcp packing for rare gas solids at high pressures.[27,29,32,33] Considering a solid rare gas at high pressure to be a polycrystalline structure, we can therefore safely assume that it consists of clusters with hexagonal close-packed structure. It would thus certainly be of interest to find the typical size of these cluster/domains. The above analysis implies that if we construct this bulk system from clusters with magic numbers (i.e., with completed shells), the average number of nearest neighbors for atoms is approximately 8.8 when individual clusters of identical size can occupy a volume inside their corresponding balls. This means that such clusters may rotate freely inside the ball volume. However, because this is valid for any ball radius, it is impossible to estimate the number of cluster atoms on the basis of the packing parameter. Only with a more elaborate model could one make such an estimate.

Thus, on the basis of recent studies, one can explain the redistribution of atoms in solid rare gases resulting from compression, in the following way. At low pressures ($p \ll p_o$), the crystal has fcc structure ($q=12$); an increase of external pressure leads to a stacking instability that starts from $p \sim p_o$. As a result of this instability, elements of hexagonal structure arise inside the crystal, at first for layers, and later for domains or small clusters. The random distribution of cluster orientations produces a decrease of the packing density φ and of the mean coordination number q of this system due to formation of voids on boundaries of regularly structured clusters. Along with this, neighboring clusters are fixed by pairwise interactions, so that at high pressures rare gases consist of small solid domains/clusters, so that a bulk solid containing a large number of such domains has an amorphous structure but short-range order. Since interaction of adjacent domains is determined in significant part by interaction of non-nearest atoms, their structure can be sensitive to the details of the interaction potential between atoms. Consequently the parameters of strongly compressed rare gases at low temperatures may be very different for different rare gases.

We see that the equilibrium solid form of a strongly compressed rare gas has some disorder, differing from the regular crystalline lattice form that is stable at low pressures. On the basis of a sum of investigations, we infer that solid rare gases at high pressures consist of small domains/clusters. The liquid state of such a system at high pressure is similar to that at low pressure, with voids spread throughout a random distribution of atoms.[34] Of course the parameters of voids at low and high pressures are different. The solid-liquid phase transition has the same nature for low and high pressures. It consists in the loss of long-range order for non-nearest atoms. (We use the term “liquid” for the low-density disordered form, even if the atomic mobility in such a phase is low.)

There is one possibility to raise here, although we have not investigated it. It is well established that clusters of rare gas atoms in the gas phase tend to have icosahedral structures, rather than close-packed lattice structures. The precise size region in which the crystalline form becomes the more stable is not known, but it is probably in the range of several thousand atoms. It is conceivable that if the domains of local order were of this size or smaller, then the structure of the locally ordered regions might be icosahedral. One might ask whether it would be possible to prepare a system with such clusters, e.g., by deposition onto a cold surface, and then subject the sample to high pressure, for studies comparable to those of Refs. 27, 29, 32, and 33.

CONCLUSIONS

Guided by investigations of condensed rare gases at high pressures and using available information about these systems and models of dense systems of atoms with repulsive nearest-neighbor interactions, we conclude that the equilibrium solid state of such a system at high pressures does not have a crystalline structure. From the sum of the investigations, we infer that the solid system of repelling atoms at high pressures consists of small solid domains, clusters of close-packed structure (fcc or hexagonal or their mixture), and each cluster is fixed in space. Hence, the solid system of strongly repelling atoms is characterized by order on the scale of typical sizes of individual clusters, but is amorphous on large scales. The corresponding parameters probably vary continuously as the pressure or temperature varies. Therefore interaction of non-nearest neighbors can be important for the solid state structure of a system of repelling atoms. Moreover, the sizes of the ordered domains may well be less than the correlation length required for scaling laws to be applicable. This means that these systems can violate the scaling law for parameters of a system of repelling atoms, which is valid at low pressures for rare gases.[16,17,31] In addition, one can see that the liquid state of a system of repelling atoms differs from that for attracting atoms and is characterized by a different number q of nearest neighbors.

One can conclude from the investigations of various properties of the system of repelling atoms that its properties are not so simple. Moreover, we have found some apparent inconsistencies or paradoxes regarding properties of this system that require additional analysis. Nevertheless, one can understand general properties of this system concerning its structure and phase transition. In particular, it follows that the properties of the aggregate states of this system differ from those of condensed rare gases at low pressures. This is one more example, in addition to the phenomenon of coexistence of phases in a finite system of simple atoms,[35–37] in which an assembly of small systems shows us a characteristic of phase transitions more complex than that customarily derived from classical thermodynamics of bulk systems.

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