

Monte Carlo study of expanded matter at low temperatures

S. M. Stishov and A. V. Smirnov*

Institute of Crystallography, Russian Academy of Sciences, 117333 Moscow, Russia

**Information and Computation Center, Kurchatov Institute Russian Science Center, 123182 Moscow, Russia*

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A system of Lennard–Jones particles at a low density and a low temperature has been studied by the Monte Carlo method in an NVT ensemble.

Under certain conditions, a spatially disordered state of the matter may have a potential energy lower than that of a crystalline state.

The expanded state of matter, corresponding to negative pressures, occurs only rarely naturally, but it does occur. States with negative pressure which are reached by slowly cooling a superheated liquid are well-known examples.¹ Of greater interest from the physics standpoint, however, is the case in which the system or subsystem is extended by internal factors, such as the electron–gas pressure in a metal and the pressure associated with a zero energy in a quantum crystal or liquid. In such cases the total pressure of the system need not necessarily be negative.

Our interest in expanded matter, i.e., in matter at a negative pressure, stems from the problem of the relative stability of the crystalline and noncrystalline (spatially disordered) states. To clarify the formulation of the problem we consider a classical system of particles interacting with a binary Lennard–Jones (6–12) potential. We imagine that we have been able to stretch out our system in such a way that the smallest distance between particles satisfies $r_1 > 1.244\sigma$, where σ and 1.244σ correspond to the vanishing of the potential $\Phi(r)$ and its second derivative $d^2\Phi/dr^2$ (Fig. 1).¹ We recall that the potential energy of the system can be written in this case as

$$E = \left\langle \frac{1}{2} \sum_{ij} \phi(r_i - r_j) \right\rangle = (N\rho/2) \int \phi(r)g(r)d^3r, \quad (1)$$

where $\phi(r)$ is the interaction potential, $g(r)$ is the radial profile of the particles, and ρ is the density.

For a crystal at $T=0$, in which case the radial profile $g(r)$ is a sum of δ -functions, and in the approximation of nearest-neighbor interactions (Fig. 1), we have $E = (N/2)\phi(r_1)Z$, where Z is the coordination number. We now spread out the δ -function and describe the distribution of nearest neighbors by a Gaussian function (Fig. 1). As the width of the Gaussian increases, the energy of the system calculated from expression (1) decreases until the tail of the Gaussian overlaps significantly with the region of strong repulsion. The physical nature of this effect is quite clear. The reason is that the derivative $d\Phi/dr$ falls off rapidly with increasing r at $r > 1.244\sigma$ (1.244σ is the inflection point). If we go through a similar procedure for the point r_2 in the region of strong repulsion, the energy of the system will obviously increase with increasing width of the distribution.

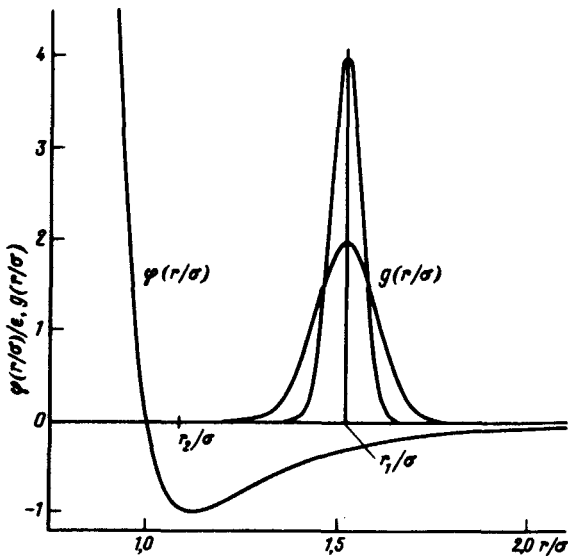


FIG. 1. Diagram used in calculating the potential energy of the Lennard-Jones system at a low density (see the text proper).

It thus seems extremely likely that the lowest-energy state in the approximation of a nearest-neighbor interaction, at a low density, will correspond to either an extremely specific crystal with static displacements of the particles from the lattice sites or a spatially disordered amorphous body. This conclusion can of course serve as only a starting point for a more accurate study of the question.

Unfortunately, the situation shown schematically in Fig. 1 is difficult to study in its pure form, without incorporating an additional interaction which stabilizes the system. Essentially any system of particles with a realistic interaction becomes unstable² at low densities, and this tendency causes difficulties in efforts to evaluate the energy of spatially disordered phases. Nevertheless, as we will see below, numerical calculations by the Monte Carlo method form a basis for drawing completely definite conclusions.

The thermodynamic properties of a system with an interaction

$$\phi(r) = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6], \quad r \leq r_c,$$

$$\phi(r) = 0, \quad r > r_c,$$

were studied by the classical Monte Carlo method in an isochoric ensemble of N particles in a cube of volume V with periodic boundary conditions. A specific realization of this simulation method is described in Ref. 3. The cutoff radius r_c is taken to be 2.5σ . Analysis shows that increasing this radius to 4.2σ does not alter the conclusions of this study.

As we have already mentioned, one of the goals of this study was to learn about the disordered state of a system of Lennard-Jones particles at temperatures close to absolute zero. Here is an outline of the calculations: A system consisting of $N=432$ particles at the sites of a crystal lattice, at a density $N/V = 0.4\sigma^{-3}$, is heated to the

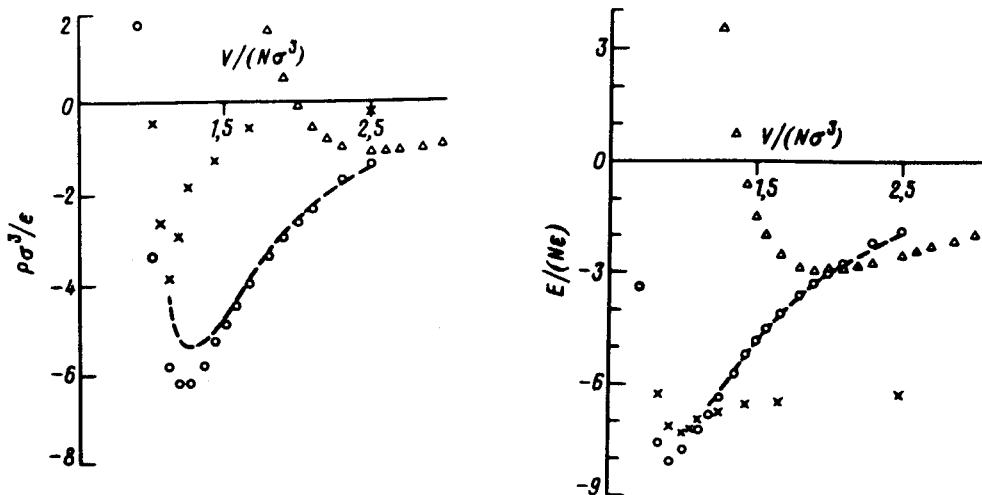


FIG. 2. The energy per particle, E/N , and the pressure P of a system of Lennard-Jones particles (the cutoff radius for the potential is $r_c = 2.5\sigma$) versus the volume V/N at $T=0$. \circ —Face-centered-cubic lattice; Δ —diamond lattice; \times —amorphous state; dashed curve—amorphous state obtained by extrapolating from the stability region (see the text proper).

point that the crystal fractures. It is then put in a state of a given density at $T = 1.0\epsilon$. It is then cooled in steps of $\Delta T = 0.1\epsilon$ to $T = 0.1\epsilon$ at a fixed density. After each cooling step, $10^3 N$ configurations are generated by the Monte Carlo method, and the next cooling step is carried out. A prolonged relaxation at $T = 0.003\epsilon$ is carried out to determine the energy and pressure of the disordered system at $T=0$: $2.5 \times 10^4 N$ configurations are generated by the Monte Carlo method. Further simulation leads to essentially no change in the average energy of the system for the densities and temperatures considered.

We believe that this procedure makes it possible to reach a disordered state with the energy closest to the lowest attainable: At normal density, the energy of the resulting amorphous state is essentially independent of how this state was prepared.³ In the case at hand, however, the energy of the amorphous phase which arises from the fracture of the fcc lattice, at $T = 0.003\epsilon$ in the region in which this phase is unstable ($N/V < 0.826\sigma^{-3}$), is about 0.3ϵ higher than the energy of the amorphous phase produced from the supercooled liquid even after a prolonged relaxation ($4 \times 10^4 N$ configuration) (a possible reason for this difference is discussed below). The radial profiles $g(r)$ for these two amorphous structures are essentially identical.

Figure 2 shows the energy as a function of the volume for an fcc lattice and a disordered (amorphous) structure. The energies of the fcc lattice were calculated analytically for $\rho = N/V < 0.826\sigma^{-3}$. The volume dependence of the energy of the amorphous phase was found through Monte Carlo calculations. It can be seen from Fig. 2 that the energy of the amorphous system changes only very slightly as the density is reduced by a factor of more than 2. This result looks questionable. The

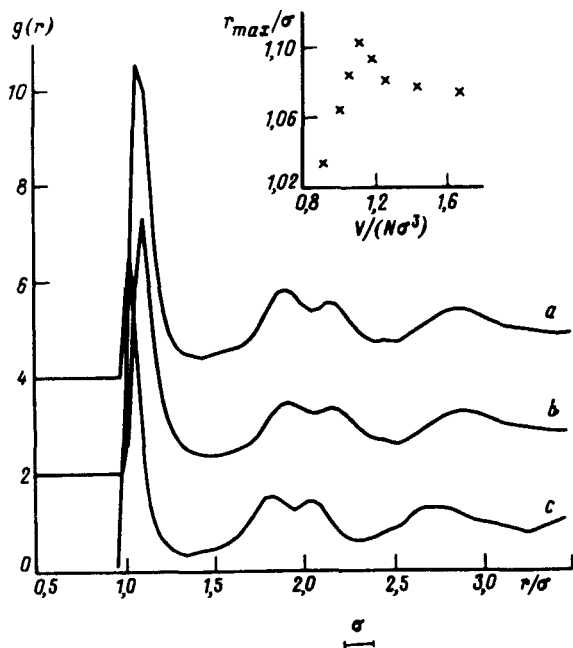


FIG. 3. Radial profiles $g(r)$ for various volumes V/N in a supercooled Lennard-Jones system at $T = 0.1\epsilon$. a — $V/N = 0.91\sigma^3$; b — $1.11\sigma^3$; c — $1.43\sigma^3$. Curves a and b have been shifted for clarity. The inset shows the position of the first peak in the radial profile, r_{\max} , versus the volume.

situation can be clarified by analyzing Figs. 3 and 4. The radial profiles $g(r)$ for the three densities considered in Fig. 3 look quite ordinary. However, the coordinate of the first maximum, r_{\max} , on the $g(r)$ curve undergoes an irregular shift as a function of the density. As the volume is increased, the distance between nearest neighbors increases, as we would naturally expect. When the values $\rho \approx 0.9$ and $\partial P/\partial V \approx 0$ are reached (Fig. 2), however, the derivative $\partial r_{\max}/\partial V$ reaches zero and then changes sign. The results are summarized by Fig. 4, which shows projections of the centers of gravity of

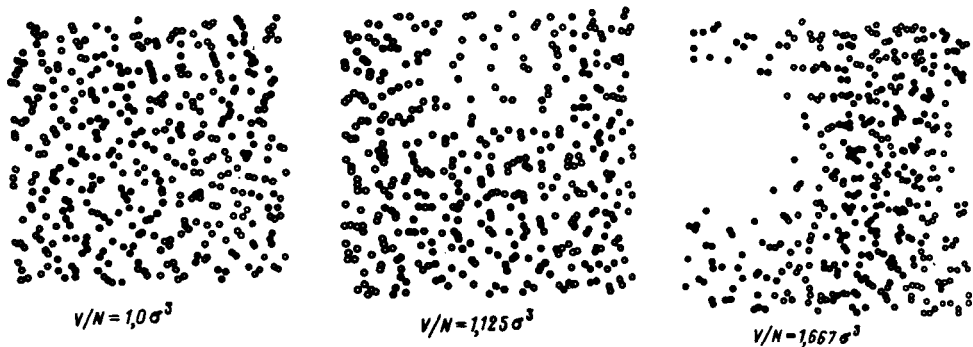


FIG. 4. Projections of the center-of-mass of particles in a Lennard-Jones amorphous system for different values of the volume ($T=0.003\epsilon$).

the particles onto the plane for various densities. We see from Figs. 2 and 4 that discontinuities form at a low density in the amorphous phase, and a "Swiss-cheese" structure arises. The interatomic distances and the pressure relax to lower values, and the effective density of the material actually increases. Similar discontinuities are observed in the amorphous phase which arises upon destruction of the fcc phase at low temperatures. The reasons for the small variation in the energy of the amorphous system with increasing volume thus become apparent. The appearance of these voids seems to explain the small difference in the energies of the amorphous phases prepared in different ways, as was pointed out earlier. The size and shape of the voids must be a factor here.

The porous low-temperature structure of the amorphous phase is essentially an analog of a high-temperature two-phase state of a substance corresponding to the coexistence of a liquid and a gas.

These results do not conflict with physical intuition. An omnidirectional expansion of a body at a low temperature results in rupture of the body when the instability condition $\partial P/\partial V > 0$ becomes satisfied at some critical density. Curiously, the rupture of an amorphous body occurs at a density higher than in the case of a crystal. The rupture evidently occurs at "weak spots."

However, as we have already mentioned, the situation of greatest interest is that in which the system is extended by internal factors. Let us imagine a case in which the energy of the binary interaction is only a fraction of the overall interaction in a system, and there exists a purely bulk contribution to the total energy of the system, E' , of the form $f(N/V)$. If the form of the function $f(N/V)$ is such that the contributions to the pressure and the bulk modulus are positive, then the state of the system may stabilize at a density $\rho < 0.9$. In this case conditions would not favor the formation of the Swiss-cheese structure, and the spatial distribution of the particles would be substantially more nearly uniform.

To determine the behavior of the binary-interaction energy as a function of the volume for this case, we extrapolated the energy of the amorphous phase out of the stability region to low densities by scaling the interparticle distances and then calculating the energy. Curiously, the results of this extrapolation are essentially independent of the initial density. The curve found in this manner seems to set an upper bound on the energy of the *relaxed* amorphous state at large volumes, while a lower bound is set by the curve characterizing the porous structure. We note that the extrapolation curve in Fig. 2 is close to the energy of the fcc phase; at large volumes it runs a bit below the latter. We thus reach the completely plausible conclusion that under certain conditions the amorphous state may serve as the ground state.²⁾

To complete this discussion of the results, we note that a "porous" diamond becomes more favorable than a close-packed or amorphous phase from the energy standpoint at low densities (Fig. 2). Since the stabilizing energy E' does not alter the relative positions of the energy levels, we easily conclude that there is the possibility in principle that the following sequence of phase transitions occurs as the density of the substance changes: "porous" crystalline phase \leftrightarrow amorphous medium \leftrightarrow dense crystalline phase. A sequence of this sort has been observed experimentally,⁵ but of course

we cannot assert that the amorphous medium observed experimentally is a stable, rather than metastable, phase.

¹⁾At $r_1 > 1.244\sigma$ the potential becomes complex.

²⁾To those who may perceive a violation of the Nernst theorem in this assertion, we would point out that the spatial disorder and the entropy are not related in a single-valued way.⁴

¹ L. D. Landau and E. M. Lifshitz, *Statistical Physics* (Pergamon, New York, 1980).

² S. M. Stishov, *Pis'ma Zh. Eksp. Teor. Fiz.* **57**, 189 (1993) [*JETP Lett.* **57**, 196 (1993)].

³ A. M. Bratkovskii and A. V. Smirnov, *Rasplavy* **1**, 32 (1990).

⁴ S. M. Stishov, *Usp. Fiz. Nauk* **154**, 93 (1988) [*Sov. Phys. Usp.* **31**, 52 (1988)].

⁵ R. J. Hemley, A. P. Jephcoat, H. K. Mao *et al.*, *Nature* **334**, 52 (1988).

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