Monte Carlo determination of the elastic constants of the hard-sphere solid

Karl J. Runge* and Geoffrey V. Chester
Laboratory of Atomic and Solid State Physics, Cornell University, Ithaca, New York 14853-2501
(Received 5 June 1987)

Monte Carlo simulation is used to study the elastic properties of the classical hard-sphere solid. The elastic constants C_{11}, C_{12}, and C_{44} are computed for the fcc lattice structure at the melting density. Poisson's ratio is computed and is shown to be positive. These "exact" results are compared with those of simple models of the hard-sphere solid.

I. INTRODUCTION

Starting with the work of Ramakrishnan and Yussouff,[1] density-functional theories have been an important development in the study of classical solids and the solid-fluid phase transition. Recently there have been explorations into the application of these theories to compute a variety of physical quantities, in particular, the elastic constants of the solid phase.[2,3] Given this state of development of the theories, we thought it was timely to compute the elastic constants of the hard-sphere solid to provide a useful benchmark for present and future theoretical treatments. As will be seen below in Sec. III, the discontinuity in the hard-sphere potential presents a few technical difficulties for the computation of the elastic constants. In spite of these problems, the hard-sphere system was chosen for the following reasons.

(1) The hard-sphere system is a convenient test bed for the density-functional theories because the exact liquid structure factor $S(k)$ (an essential ingredient of the theories) is accurately described by the Verlet-Weis[4] modification of the analytical solution to the Percus-Yevick equation for hard spheres.

(2) The elastic properties of the hard-sphere solid are nontrivial in the sense that, due to the discontinuous nature of the potential, there are no "static lattice" or "harmonic" treatments of the elastic constants. Thus this work will provide the elastic constants of a highly anharmonic solid.

(3) Jarić and Mohanty[3] have performed a density-functional computation of the elastic moduli of the hard-sphere crystal and have arrived at the result that Poisson's ratio is negative. Their work, in fact, was the primary stimulus for this computation.

In Sec. II a fairly careful definition of the isothermal elastic constants is given. Care is taken since nearly all treatments of elastic moduli assume zero initial stress, which is, of course, impossible for the purely repulsive hard-sphere system. The generalization of Poisson's ratio is anisotropic crystals is also discussed in this section.

Section III is devoted to the description of the Monte Carlo method used to estimate the elastic constants. The difficulties presented by the hard-sphere potential are discussed here, along with possible ways to avoid them.

In Sec. IV we present our results for the elastic moduli C_{11}, C_{12}, and C_{44}; the pressure P; and the inverse compressibility $(\partial P/\partial\rho)_T$ at the melting density. The errors in these quantities are discussed. The moduli are then used to compute the "generalized" Poisson's ratio for the system. Lastly, we compare the computed elastic constants with the predictions of a free-volume theory and a simple static lattice model.

II. DEFINITION OF THE ELASTIC CONSTANTS

Let $\mathbf{x}$ denote the position of a material point in the solid in the undeformed state. Next, let $u_i(\mathbf{x})$ be the displacement of the material point in the ith direction after the deformation has taken place. The nonlinear Lagrangian strain tensor η_{ij} describes the state of deformation of the system and is defined by

$$\eta_{ij}=\frac{1}{2}\left[\frac{\partial u_i}{\partial x_j}+\frac{\partial u_j}{\partial x_i}+\frac{\partial u_k}{\partial x_i}\frac{\partial u_k}{\partial x_j}\right], \tag{1}$$

where $1\le i,\ j\le 3$, and the Einstein summation convention is in force throughout this paper: repeated indices are summed over. In computing the elastic constants we assume that the strain is homogeneous, in other words, η_{ij} is independent of $\mathbf{x}$. For a more complete discussion of the above see Wallace.[5]

Now define the Helmholtz free energy F by

$$F=-k_BT\ln Z\ , \tag{2}$$

where k_BT is Boltzmann's constant times the temperature and Z is the canonical partition function of the system. Z depends on the number of particles N, the temperature T, the size and shape of the container, and the boundary conditions. Periodic boundary conditions were used exclusively in this work. For small enough strain, plastic flow will not occur and so displacing the boundary surfaces by an amount corresponding to the strain η_{ij} should give rise to a similar transformation of the crystal's unit cell. Under these conditions the free energy should be a smooth function of the strain and we may write

$$Z=Z(N,V,\eta_{ij},T)=\frac{1}{N!\Lambda^{3N}}Q(N,V,\eta_{ij},T)\ ,$$

where

$$Q=\int_{V'} d\mathbf{r}_1 \int_{V'} d\mathbf{r}_2 \cdots \int_{V'} d\mathbf{r}_N \exp[-\beta U(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_N)] , \tag{3}$$

$\mathbf{r}_i$ is the position of the ith particle, $1\leq i\leq N$; $\beta=1/k_BT$; Λ is the deBroglie thermal wavelength;[6] and U is the potential energy of interaction of the particles. The integrals over V' indicate that the coordinates are to range over the entire *deformed* volume. The only way the strain, η_{ij}, enters into the partition function is through these integration limits.

If we let f denote the free energy per particle, $f=F/N$, and let ρ be the number density of the undeformed state, $\rho=N/V$, then we are in a position to define the elastic constants. The constants are defined as the coefficients in the following expansion of ρf about $\eta_{ij}=0$:

$$\rho f(\eta_{ij})=\rho f(0)+T_{ij}\eta_{ij}+\tfrac{1}{2}C_{ijkl}\eta_{ij}\eta_{kl}+\cdots , \tag{4}$$

where the N,V,T dependence has been suppressed in f, T_{ij}, and C_{ijkl}. All repeated indices are summed over. T_{ij} is the stress tensor: the component T_{ij} is the force per unit area in the ith direction acting across an area element perpendicular to the jth direction. The C_{ijkl} are the isothermal elastic constants we wish to calculate.

One can see from Eq. (4) that there is a subtlety in the definition of C_{ijkl} when the initial stresses are not all zero. Since the strain tensor is assumed to be small, one may argue that the third term in Eq. (1) is of higher order and so one may just as well take the following as the strain tensor:

$$\epsilon_{ij}=\frac{1}{2}\left[\frac{\partial u_i}{\partial x_j}+\frac{\partial u_j}{\partial x_i}\right] . \tag{5}$$

In fact, if *all* of the T_{ij} are zero then both definitions, (1) and (5), give rise to exactly the same C_{ijkl}. However, if some of the T_{ij} are not zero then, in Eq. (4), the "terms of higher order" in $T_{ij}\eta_{ij}$ clearly modify the next-order term, $\frac{1}{2}C_{ijkl}\eta_{ij}\eta_{kl}$. We will use definition (1) as the strain in this paper. While the above discussion is based purely on definitions, it clarifies exactly what is meant by "C_{ijkl}."

From the above one can show

$$\begin{aligned}&\eta_{ij}=\eta_{ji},\quad T_{ij}=T_{ji} ,\\ &C_{ijkl}=C_{jikl}=C_{klij}=\cdots .\end{aligned} \tag{6}$$

We will use the standard Voigt notation in this paper; it is a mapping of two indices (ij) onto one (α):$11\rightarrow 1$; $22\rightarrow 2$; $33\rightarrow 3$; $12,21\rightarrow 4$; $23,32\rightarrow 5$; and $31,13\rightarrow 6$. If the undeformed system has cubic symmetry, as does the face-centered-cubic (fcc) crystal considered here, then one can easily show that a large number of the expansion coefficients in Eq. (4) vanish. In the Voigt notation, the only nonzero stresses are T_1, T_2, and T_3. Furthermore, $T_1=T_2=T_3=-P$, which implies the stress tensor is equal to the negative of the isotropic pressure times the identity matrix. For a system with cubic symmetry, of the $6\times 6=36$ possible $C_{\alpha\beta}$, only 12 are nonzero, and among these there are only three independent ones, which can be taken as C_{11}, C_{12}, and C_{44}.[5]

We conclude this section with a short discussion of Poisson's ratio. For an isotropic system, Poisson's ratio σ_p is the negative of the ratio of the transverse strain to the longitudinal strain when the stress is incremented parallel to the longitudinal direction.[7] Thermodynamic considerations restrict Poisson's ratio to lie between -1 and $\frac{1}{2}$ for an isotropic system. If σ_p is less than zero, then when one stretches the material in one direction it *expands* at right angles to this direction. In general one believes that materials have $\sigma_p>0$, but there are some notable exceptions.[8] For an anisotropic solid, Poisson's ratio depends on both the direction along which the increment in stress is made and the direction along which the resulting contraction is measured. If the stress is incremented along $\hat{\mathbf{n}}$ then it is sufficient to know σ_p for two mutually orthogonal directions, both perpendicular to $\hat{\mathbf{n}}$: the σ_p associated with contraction along any other direction may be obtained by the standard rules for rotating tensors. The knowledge of the elastic constants and initial stresses coupled with the general stress-strain relations enables one to compute σ_p along an arbitrary direction in the crystal for any transverse direction. All of this is discussed in detail in Wallace.[5]

III. COMPUTATIONAL METHOD

The method used in this work to compute the elastic constants is that of Broughton,[9] with slight modifications required to treat the discontinuous nature of the hard-sphere interaction. The method involves performing a Monte Carlo simulation of a system which has a small, finite strain applied to it. The strain is imposed by constraining each particle to remain inside the deformed volume V' in Eq. (3). During the course of the simulation the stress tensor of the *deformed* system is measured. The linear dependence of this stress tensor on the (small) strain is then used to "pick out" the elastic constants of the undeformed system. Specifically, consider the system in the state of deformation given by η_{ij}. By using Eq. (4) and considering infinitesimal changes in the strain about the deformed state, one arrives at the following expression for the stress tensor in the deformed state:

$$T_{ij}(\{\eta\})=T_{ij}(0)(1-\eta_{kk})+C_{ijkl}(0)\eta_{kl}+O(\eta^2) , \tag{7}$$

where $\{\eta\}$ implies "in the deformed state" and we have explicitly put "(0)" to signify that the quantity pertains to the undeformed state. The factor multiplying $T_{ij}(0)$ comes from the change in the overall factor of ρ in Eq. (4). Given that one can perform simulations to estimate $T_{ij}(\{\eta\})$ and $T_{ij}(0)$, one proceeds to do so at the number of distinct strains necessary to solve the set of linear equations [Eq. (7) applied to each $\{\eta\}$] for the elastic constants $C_{ijkl}(0)$. Thus if there are n independent elastic constants, one must perform at least $n+1$ simulations with different strains: one at zero strain to get

$T_{ij}(0)$, and then n more at distinct values of strain to pick off the $C_{ijkl}(0)$. It is also a good idea to do additional simulations in which the strain is merely scaled up or down by a factor to test if one is actually in the linear regime of Eq. (7).

We now specialize to the case of cubic symmetry, and shall shortly specialize to the hard-sphere system. For a cubic crystal under isotropic pressure one has, from Wallace,

$$\rho\left[\frac{\partial P}{\partial \rho}\right]_T = \tfrac{1}{3}(C_{11}+2C_{12}+P) \ . \tag{8}$$

In our work the pressure was computed in the standard fashion[10] at three densities; ρ, $\rho+\delta\rho$, and $\rho-\delta\rho$. The pressures from the last two densities allow one to estimate $\partial P/\partial\rho$ at ρ by finite differencing. Equation (8) gives one piece of information and so two additional Monte Carlo simulations must be performed with different types of strain to extract the three independent elastic constants. We have tried to choose these strains to minimize errors and maximize convenience as much as possible.

For lack of a better terminology, we label the two strains "shear 1" and "shear 2." Shear 1 is defined by the following transformation of coordinates:

$$\begin{aligned} x' &= x+\epsilon y \ , \\ y' &= y \ , \\ z' &= z \ , \end{aligned} \tag{9}$$

and shear 2 by

$$\begin{aligned} x' &= (1-\epsilon)x \ , \\ y' &= (1+\epsilon)y \ , \\ z' &= z \ . \end{aligned} \tag{10}$$

In both cases ϵ is a parameter which determines the magnitude of the strain, with, of course, $\epsilon=0$ implying no deformation. Shear 1 is seen to be a simple shear parallel to the xz plane. Shear 2 can be shown to be a composite of two simple shears.[7]

An important point to note is that the above two strains are "invariant" when ϵ is replaced by $-\epsilon$. This invariance follows from the cubic symmetry: for shear 1 one uses $y\leftrightarrow -y$ and for shear 2 one uses $(x,y)\leftrightarrow(y,x)$. Thus the free energy per particle is an even function of ϵ: $f(\epsilon)=f(-\epsilon)$ for both shears. This fact is of great convenience, for it implies

$$\frac{\partial f}{\partial \epsilon}(\epsilon) = \frac{\partial^2 f}{\partial \epsilon^2}(0)\epsilon + O(\epsilon^3) \ , \tag{11}$$

which is a useful piece of information since we will be trying to extract the linear term of this expression. The lack of a zeroth-order term in (11) is desirable because we avoid increasing our statistical error by having to subtract off the constant. The absence of an $O(\epsilon^2)$ term is equally convenient since it makes it much easier to be in the linear regime of Eq. (11).

We shall now describe how to compute the left-hand side of Eq. (11) for the hard-sphere system. The configurational integral of the system is

$$Q = \int_{V'} d\mathbf{r}_1 \cdots \int_{V'} d\mathbf{r}_N \prod_{(i,j)} \Theta(r_{ij}-\sigma) \ , \tag{12}$$

where $r_{ij}=|\mathbf{r}_i-\mathbf{r}_j|$ and σ is the hard-sphere diameter. The theta function, $\Theta(x)$, is 1 if $x\geq 0$ and 0 otherwise. Let ϵ_1 be the strain parameter of shear 1 and, similarly, let ϵ_2 correspond to shear 2. Use of Eq. (2) and the strain definitions, (9) and (10), leads to

$$\frac{1}{k_B T}\frac{\partial f}{\partial \epsilon_1}(\epsilon_1) = -\frac{1}{N}\left\langle \sum_{(i,j)} \delta(r_{ij}-\sigma)\frac{x_{ij}y_{ij}}{r_{ij}} \right\rangle_{\epsilon_1} \ , \tag{13}$$

and

$$\frac{1}{k_B T}\frac{\partial f}{\partial \epsilon_2}(\epsilon_2) = \frac{2\epsilon_2}{1-(\epsilon_2)^2} - \frac{1}{N}\left\langle \sum_{(i,j)} \delta(r_{ij}-\sigma)\frac{1}{r_{ij}}\left[\frac{y_{ij}^2}{1+\epsilon_2}-\frac{x_{ij}^2}{1-\epsilon_2}\right] \right\rangle_{\epsilon_2} \ , \tag{14}$$

where x_{ij}, y_{ij}, and z_{ij} are the three components of $\mathbf{r}_i-\mathbf{r}_j$, and $\delta(x)$ is the Dirac delta function. The average of an observable A is defined by

$$\langle A \rangle_{\epsilon_\nu} = \frac{1}{Q(\epsilon_\nu)} \int_{V(\epsilon_\nu)} d\mathbf{r}_1 \int_{V(\epsilon_\nu)} d\mathbf{r}_2 \cdots \int_{V(\epsilon_\nu)} d\mathbf{r}_N \, A(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_N) \prod_{(i,j)} \Theta(r_{ij}-\sigma) \ , \tag{15}$$

where $V(\epsilon_\nu)$ denotes the volume of the deformed container under strain ϵ_ν ($\nu=1,2$), and $Q(\epsilon_\nu)$ is the corresponding value of the partition function. Formulas (13) and (14) are derived in the standard manner in which one computes the virial expression for the pressure.[11] One introduces a change of variables in the integral (12) such that the integration limits do not change with ϵ_ν, but rather the integrand contains all of the dependence. The single differentiation of the integrand with respect to ϵ_ν is then carried out, and the above formulas are obtained by making a change of variables back to the original integration coordinates.

The delta functions in expressions (13) and (14) cannot be averaged directly from the configurations generated in the Monte Carlo simulation. Rather, one breaks up the pair separation r_{ij} into "bins" of width Δr and averages the coefficient of the delta function for each bin. One then extrapolates the bin averages to $r_{ij}=\sigma$. This technique is completely analogous to the standard method of estimating the virial pressure for the hard-sphere system.[10] The procedure is awkward and the extrapolation increases the error in the estimates, so a method was

developed that avoids extrapolation altogether. The technique involves the construction of an estimator for the stress based on an analytic expression for the expected value of a "fictitious" Monte Carlo step. Details are presented in the Appendix. Unfortunately, the simple implementation of the method used in this work can be shown to have infinite variance. Although appearing to be disastrous, this fact did not prevent the new estimators from providing very useful checks of the standard extrapolation method.

IV. RESULTS AND DISCUSSION

All of the results presented in this section are given in reduced units where the hard-sphere diameter σ is taken as the unit of length and energies are measured in units of $k_B T$. The system consisted of 500 hard spheres at the established melting density, $\rho = 1.040\,86$.[12] "Spot checks" of the effect of finite size were done with systems of 256 and 864 particles. Any statistically significant size dependence was extrapolated to $N = \infty$ assuming an $O(1/N)$ correction term. The shape of the undeformed simulation cell was a cube, and the particles obeyed periodic boundary conditions.

Table I contains the results of the computation of the pressure and finite-differenced compressibility. A "pass" in the Monte Carlo simulation is defined to be one attempted move of every particle in the system. In the runs of Table I the system was started in a perfect fcc crystal and then allowed to relax for 5000 passes. Information used to determine the pressure was then collected over the next 300 000 passes. Runs of this length gave an accuracy in the pressures of about 0.1%, which was satisfactory for the purposes of the paper.

From Eqs. (1), (4), (9), and (10) one can derive the following expressions:

$$\mu_1 \equiv \frac{\rho}{\epsilon_1}\frac{\partial f}{\partial \epsilon_1}(\epsilon_1) = (C_{44} - P) + O(\epsilon_1^2) \tag{16}$$

and

$$\mu_2 \equiv \frac{\rho}{\epsilon_2}\frac{\partial f}{\partial \epsilon_2}(\epsilon_2) = 2(C_{11} - C_{12} - P) + O(\epsilon_2^2)\ . \tag{17}$$

The quantities μ_1 and μ_2 are found by using the Monte Carlo estimates of the right-hand sides of Eqs. (13) and (14), respectively. As mentioned in the previous section, μ_1 and μ_2 can be computed by extrapolating certain "bin averages," which are now described. Let $\mu_1(\bar{r})$ denote $(\rho/\epsilon_1 \Delta r)$ times the average of the coefficient of the delta function in Eq. (13) for all pairs with separation between $\bar{r} - \frac{1}{2}\Delta r$ and $\bar{r} + \frac{1}{2}\Delta r$. Similarly, let $\mu_2(\bar{r})$ correspond to the same quantity for shear 2. By assuming $\mu_\nu(\bar{r})$ varies smoothly with $\bar{r}$ one may extrapolate the bin averages to obtain μ_ν. Figure 1 shows the results for the bin averages of shear 1 with $\epsilon_1 = 0.02$. The extrapolations were performed by evaluating a quadratic fit to the first three bin averages at $\bar{r} = \sigma$. Consistency was checked by redoing the fit with the bin width doubled, and by using both bin sizes to extrapolate away the $O(\Delta r^3)$ error term. For both types of checks the estimated systematic error was found to be much smaller than the statistical error. Furthermore, the elastic moduli and pressures that were computed from the estimators requiring no extrapolation (see the Appendix) agreed with the extrapolated values quoted in this paper to within the observed error bars. The program was also tested by running in the fluid phase at $\rho = 0.7$ and the results for μ_1 and μ_2 were consistent with the fluid being unable to support a shear (which corresponds to $\mu_1 = 0$ and $\mu_2 = 2P$). In the solid runs, the system was always started from the perfect crystal obtained by straining the fcc lattice by the corresponding ϵ_ν. Typically, the initial 5000 passes were discarded and averages were computed over the next 100 000–300 000 passes.

Table II contains the extrapolated bin averages of the quantities μ_1 and μ_2 along with their standard errors for three values of the strain parameter. The $O(\epsilon^2)$ dependence in Eqs. (16) and (17) cannot be discerned from the statistical error. In Table III the finite-size dependencies of the pressure and the elastic constants are presented. Also presented in Table III are the results of the free-volume theory. In this theory each sphere is allowed to wander about in the cage defined by fixing its neighbors

TABLE I. Data used to compute the pressure and inverse compressibility of the $N = 500$ hard-sphere fcc solid.

ρ	P	$\rho\left[\frac{\partial P}{\partial \rho}\right]$
1.020 86	10.899±0.01	37.3±1.2
1.040 86	11.671±0.01	42.3±0.3
1.060 86	12.524±0.01	47.4±1.1

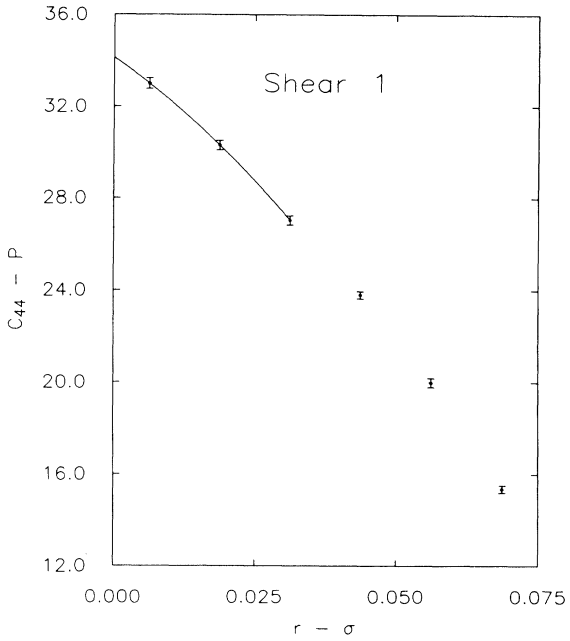

FIG. 1. Bin averages of the elastic $\mu_1 = C_{44} - P$ for $\rho = 1.040\,86$, $\epsilon = 0.02$. The estimated value for the elastic constant is the intercept at $r - \sigma = 0$. The curve is the quadratic fit used to find the intercept.

at their lattice positions.[13] Let $v_f(\rho,\epsilon)$ denote the free volume this "wandering" particle may sweep out at density ρ and strain ϵ. The configurational integral, (12) is approximated by

$$Q \approx v_f^N ,$$

which implies

$$f \approx -k_B T \ln v_f(\rho,\epsilon) . \tag{18}$$

One may next work out the pressure, inverse compressibility, and elastic moduli by taking the appropriate derivatives of v_f with respect to ρ or ϵ. For the density dependence of v_f with $\epsilon=0$ Buehler's analytic expression was used.[13] The ϵ dependence was computed by the use of a crude Monte Carlo scheme that unformly filled a cube known to contain the free volume with roughly 10^7 random points. The fraction of points falling inside the free volume provides an estimate of v_f. As is well known,[14] the simple free-volume theory gives surprisingly good results for the pressure and compressibility even at the melting density (the theory is asymptotically exact for the equation of state as the density approaches close packing: $\rho \to \sqrt{2}$). The free-volume predictions of the elastic moduli μ_1 and μ_2 are, however, less satisfactory. The most obvious difference occurs for the shear-2 modulus μ_2, which is almost three times too large. (There is some indication of singular behavior in the ϵ derivatives of the free volume at $\epsilon=0$, in which case this free-volume model would be inapplicable.) It would be interesting to see if the correlated cell theories, such as the one due to Hardy and Day,[15] give more reasonable predictions.

Finally, in Table IV we present the results for Poisson's ratio along three symmetry directions, $\hat{\mathbf{n}}$, in the crystal. As was mentioned in Sec. II, for each $\hat{\mathbf{n}}$ one must compute Poisson's ratio along two mutually orthogonal directions in the plane transverse to $\hat{\mathbf{n}}$. These two directions shall be denoted by $\|$ and $\perp$. $\|$ corresponds to the direction in the plane containing $\hat{\mathbf{n}}$ and the z axis, and $\perp$ is orthogonal to both $\hat{\mathbf{n}}$ and $\|$. For example, if $\hat{\mathbf{n}}$ is [110] then $\|$ is [001] and $\perp$ is $[\bar{1}10]$. Since the pressure of the hard-sphere system is directly proportional to the temperature, it is a simple matter to convert the isothermal elastic constants to ones for adiabatic processes (constant entropy). The conversion is given by

$$\begin{aligned} C_{11}^S &= C_{11}^T + \Delta , \\ C_{12}^S &= C_{12}^T + \Delta , \\ C_{44}^S &= C_{44}^T , \end{aligned} \tag{19}$$

TABLE II. Extrapolated bin averages of the elastic constants for the $N=500$ particle system at various values of the strain parameter ϵ. ($\rho=1.040\,86$.)

ϵ	μ_1	μ_2
0.01	33.7±0.7	82.1±1.0
0.02	34.1±0.5	84.2±0.8
0.04	34.8±0.3	83.6±0.5

where

$$\Delta = \frac{2}{3}\left[\frac{P^2}{\rho k_B T}\right] ,$$

and the superscripts S and T refer to adiabatic and isothermal processes, respectively. Poisson's ratios for both types of processes are shown in Table IV. Evidently, the isothermal $\sigma_p(\perp)$ is slightly negative along the [110] direction. This implies that if the sample is compressed along [110] then there will be a slight contraction in the $[\bar{1}10]$ direction. The contraction is more than compensated by the large expansion that occurs in the [001] direction. It is obvious that the sum of $\sigma_p(\|)$ and $\sigma_p(\perp)$ provides a measure of the overall change in area in the transverse plane when the stress is incremented along $\hat{\mathbf{n}}$. In all cases considered here the sum of the two Poisson ratios has been found to be positive.

To test the Monte Carlo result that $\sigma_p(110,\perp)<0$, a simple lattice model was used. The goal was to come up with *any* reasonable physical system that possessed a negative $\sigma_p(110,\perp)$. As shall be seen below, it is somewhat amazing that the lattice model does much better than the free-volume model in predicting the Poisson's ratios. The lattice model consists of a system of particles interacting via a pair potential $v(r)=\epsilon(\sigma/r)^n$. At $T=0$ one may compute the elastic constants and Poisson's ratios easily because the particles are localized at the fcc lattice sites. Now consider the hard-sphere limit ($n \to \infty$) of these quantities. At finite n, all of the elastic constants and the pressure have exactly the same density dependence [equal to $\epsilon(\sigma/d)^n$ for large n, where d is the nearest-neighbor distance], which cancels out of the Poisson's ratio. Therefore the Poisson's ratios approach finite values independent of the density as $n \to \infty$. The results of this "model" are presented for $n=12$ and $n=\infty$ in Table IV. Several points may be noted. First, the $n=12$ static lattice has $\sigma_p(110,\perp)<0$. This suggests that the similar result from the Monte Carlo runs is not unreasonable. Second, the hard-sphere limit ($n \to \infty$) of this model is remarkably close to the simulation results. Although the model is a *drastic* approximation to the actual hard-sphere system, evidently enough information remains about how particles rearrange under stress to allow for semiquantitative agreement. Lastly, it must be noted that the model has a severe defect in that any distinction one would hope to make between the isothermal and adiabatic elastic constants was lost when the limit $T \to 0$ was taken.

V. SUMMARY

In this study the elastic moduli and generalized Poisson's ratios have been computed to roughly 1% accuracy at the melting density for the fcc hard-sphere system. These data allow all of the elastic properties of the solid to be computed: one may derive the stress-strain relations, the acoustic wave propagation velocities and polarization vectors, etc. For compressions along the [100] and [111] directions Poisson's ratio was found to be positive, which agrees with one's physical intuition about the system. Along the [110] direction, (iso-

TABLE III. Finite-size dependence of the pressure and the elastic constants of the solid at $\rho=1.040\,86$. The last line contains the results of the free-volume theory described in the text.

N	P	$\rho\left(\frac{\partial P}{\partial \rho}\right)$	μ_1	μ_2
256	11.640±0.01	41.9±0.4	33.7±0.4	81.1±0.8
500	11.671±0.01	42.3±0.3	34.1±0.5	84.2±0.8
864	11.668±0.01	42.6±0.3	...	...
∞	11.687±0.02	42.9±0.4	34.1±0.5	83.3±0.8
free volume	10.87	43.97	43.3±0.4	229.0±9.0

thermal) compressions shall cause a slight contraction along the $[\bar{1}10]$ direction and a larger expansion along [001].

The free-volume theory gives rather disappointing predictions for the shear moduli in light of its success for the equation of state. Surprisingly, a *very* simple, $T=0$, static lattice model gives quite accurate results for the isothermal Poisson's ratios. It would be interesting to see if any extensions of the lattice model would give an even better description of the elastic properties (such as the computation of the adiabatic Poisson's ratios). It is hoped that the results of this study shall provide a useful test case for any theories attempting to compute the elastic moduli of the hard-sphere system or more complicated solids.

Note added. After the completion of this work, we obtained the results of a density-functional study by Velasco and Tarazona.[16] By extrapolating their results to the density we have worked at, it appears that their values of C_{11}, C_{12}, and $\sigma_p(100)$ are in very good agreement with ours. The value of $C_{44}-P$ they obtain (≈ 58) is 70% in excess of ours. However, we have been informed by the above authors that they are presently improving their calculation and expect significant changes in their value of C_{44}. We are performing Monte Carlo simulations at one of the densities they have studied to provide a better comparison between our results and theirs.

ACKNOWLEDGMENTS

P. W. Leung and N. W. Ashcroft are to be thanked for very useful discussions on the elastic properties of crystals. We are indebted to K. E. Schmidt for being instrumental in coming up with the Monte Carlo estimator described in the Appendix. Most of all, we would like to thank C. L. Henley, who stimulated this work by providing us with the density-functional results of Jarić[3] along with encouragement during all phases of this study. This research was supported by the National Science Foundation (NSF) under Grant No. DMR-85-13300 and was conducted using the supercomputing resources of the Center for Theory and Simulation in Science and Engineering at Cornell University, which receives funding in part from the National Science Foundation, New York State, and the IBM Corporation.

APPENDIX

In this appendix an estimator to compute averages of the form

$$\bar{h}_i \equiv \left\langle \sum_{j\ (\neq i)} \delta(r_{ij}-\sigma)h(\mathbf{r}_{ij}) \right\rangle \tag{20}$$

for the hard-sphere system is presented. The estimator avoids the extrapolation process described in Secs. III and IV.

First, define the bin average by

$$\bar{h}_{i,\mathrm{bin}} \equiv \left\langle \frac{1}{\Delta r} \sum_{j\ (\neq i)} \Theta(r_{ij}-\sigma,\Delta r)h(\mathbf{r}_{ij}) \right\rangle , \tag{21}$$

where $\Theta(x,\Delta r)$ is equal to 1 if $0\le x\le \Delta r$ and is zero otherwise. The region where $\Theta(r_{ij}-\sigma,\Delta r)=1$ defines a spherical shell of thickness Δr about particle j. In the following we will assume that

TABLE IV. Poisson's ratio along three directions in the fcc hard-sphere solid at the melting density. Results for both isothermal and adiabatic processes are given along with the free-volume predictions. The static lattice results are included with the isothermal quantities. Due to the cubic symmetry of the system $\sigma_p(\|)=\sigma_p(\perp)$ for the [100] and [111] directions.

	[100]	[110],$\|$	[110],$\perp$	[111]
		σ_p, isothermal		
Monte Carlo	0.344±0.002	0.552±0.008	−0.054±0.009	0.186±0.004
Free volume	0.077±0.015	0.070±0.015	0.165±0.010	0.129±0.003
Lattice $n=12$	0.425	0.824	−0.116	0.288
Lattice $n\to\infty$	0.333	0.500	0.000	0.200
		σ_p, adiabatic		
Monte Carlo	0.445±0.001	0.748±0.009	0.066±0.009	0.380±0.002
Free volume	0.311±0.008	0.276±0.016	0.389±0.014	0.338±0.002

$$\lim_{\Delta r \to 0} \bar{h}_{i,\mathrm{bin}} = \bar{h}_i \ .$$

Consider a configuration of the system drawn from an equilibrium ensemble by the standard Metropolis algorithm.[17] One is, of course, allowed to do one more Metropolis Monte Carlo step of the ith particle before performing the average in Eq. (21). This last step is chosen from a valid Metropolis transition probability for which one can *analytically* compute the probability of moving to the region where $\Theta = 1$. One can then obtain an expression for the expected contribution to (21) from taking this last Monte Carlo step.[18] Finally, one takes the limit $\Delta r \to 0$ of the analytic expression to arrive at an estimator for $\bar{h}_i$ that involves no extrapolation.

Most likely, a very good estimator results from a transition probability which uniformly samples the available volume surrounding the initial point $\mathbf{r}_i$ (i.e., the region of space containing the ith particle's initial position that does not intersect with any other sphere). In this case the estimator for $\bar{h}_i$ would involve the ratio of the surface area of the available volume to the available volume since Δr times this ratio is the probability of moving to the shell in which $\Theta = 1$. The computation of the above surface area and volume is a rather tedious geometry problem we chose to avoid [not to mention the average of $h(\mathbf{r})$ over the surface].

The method used here involves the following transition probability for particle i.

(1) Sample a random direction $\hat{\mathbf{u}}$.

(2) Move particle i along $+\hat{\mathbf{u}}$ until contact with another sphere is made. Call this sphere the "+" sphere and the distance moved l_+.

(3) Do the same as step (2) in the $-\hat{\mathbf{u}}$ direction. Call this sphere the "−" sphere and the distance moved l_-.

(4) Choose the new position of particle i at random uniformly on the line segment of length $l = (l_+ + l_-)$ that connects the points of contact with the + and − spheres.

One can show that this transition probability satisfies detailed balance and is therefore an acceptable choice for the Metropolis algorithm. It is a simple geometry problem to compute the expected contribution of step (4) to Eq. (21). The result for the pressure is

$$P = \rho k_B T \left\langle 1 + \frac{1}{N} \sum_{i=1}^{N} \vartheta_i \right\rangle , \tag{22}$$

where

$$\vartheta_i = \frac{1}{6} \left[\frac{1}{|\cos(\theta_+)|} + \frac{1}{|\cos(\theta_-)|} \right] \frac{1}{l} ,$$

and $\theta_\pm$ is the angle between $\hat{\mathbf{u}}$ and the relative separation *at contact* for the + and − spheres. Analogous expressions may be derived for the shear moduli μ_1 and μ_2. One may, of course, improve one's statistics by sampling a number of random directions for each particle (15 were used in this work). Unfortunately, ϑ_i is an unbounded estimator since both the cosines and the length of the line segment can go to zero. In fact, one may show that both types of singularities lead to logarithmically diverging terms in the variance of ϑ_i. This difficulty may be removed by considering the estimator involving the entire available volume mentioned above or by the method of "reselection."[19] Neither consideration was implemented in this work. Curiously, in the extensive computations performed here (over 10^9 directions sampled), although many non-Gaussian, "outlier" points were observed, in all cases the averages computed from (22) agreed with their extrapolated counterparts to within the error estimate of the latter. This observation strongly suggests that the weakness of the logarithmic divergence actually allows one to obtain meaningful averages from (22).

---

*Present address: Courant Institute of Mathematical Sciences, New York University, 251 Mercer Street, New York, NY 10012.

[1]T. V. Ramakrishnan and M. Yussouf, Phys. Rev. B **19**, 2775 (1979).

[2]M. D. Lipkin, S. A. Rice, and U. Mohanty, J. Chem. Phys. **82**, 472 (1985).

[3]M. V. Jarić and U. Mohanty, Phys. Rev. Lett. **58**, 230 (1987).

[4]L. Verlet and J. J. Weis, Phys. Rev. A **5**, 939 (1972).

[5]D. C. Wallace, in *Solid State Physics,* edited by H. Ehrenreich, F. Seitz, and D. Turnbull (Academic, New York, 1970), Vol. 25, p. 301.

[6]J. P. Hansen and I. R. McDonald, *Theory of Simple Liquids* (Academic, London, 1976).

[7]R. P. Feynman, R. B. Leighton, and M. Sands, *The Feynman Lectures on Physics* (Addison-Wesley, Reading, Mass., 1964), Vol. II, Chaps. 38 and 39.

[8]R. Lakes, Science **235**, 1038 (1987); A. E. H. Love, *A Treatise on the Mathematical Theory of Elasticity,* 4th ed. (Dover, New York, 1944).

[9]J. Q. Broughton, G. H. Gilmer, and J. D. Weeks, Phys. Rev. B **25**, 4651 (1982).

[10]J. A. Barker and D. Henderson, Mol. Phys. **21**, 187 (1971).

[11]T. L. Hill, *Statistical Mechanics* (McGraw-Hill, New York, 1956).

[12]D. Frenkel and A. Ladd, J. Chem. Phys. **81**, 3188 (1984).

[13]R. J. Buehler, R. H. Wentorf, Jr., J. O. Hirschfelder, and C. F. Curtiss, J. Chem. Phys. **19**, 61 (1950).

[14]B. J. Alder, W. G. Hoover, and D. A. Young, J. Chem. Phys. **49**, 3688 (1968).

[15]R. J. Hardy and M. A. Day, Phys. Rev. B **29**, 4108 (1984).

[16]E. Velasco and P. Tarazona, Phys. Rev. A **36**, 979 (1987).

[17]N. Metropolis, A. W. Rosenbluth, M. N. Rosenbluth, A. H. Teller, and E. Teller, J. Chem. Phys. **21**, 1087 (1953).

[18]M. H. Kalos and P. Whitlock, *Monte Carlo Methods* (Wiley, New York, 1986), Vol. I, pp. 103–107.

[19]H. A. Steinberg and M. H. Kalos, Nucl. Sci. Eng. **44**, 406 (1971).