CMST 8(2) 84-92 (2002) DOI:10.12921/cmst.2002.08,02.84-92

COMPUTATIONAL METHODS IN SCIENCE AND TECHNOLOGY **8(2)**, 84-92 (2002)

ELASTIC PROPERTIES OF THE f.c.c. HARD SPHERE CRYSTAL FREE OF DEFECTS

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Abstracts. Elastic properties of the f.c.c. phase of hard spheres are determined by Monte Carlo simulations of the box fluctuations in the constant pressure ensemble with variable box shape (NpT). It is shown that the extrapolated data differ by only a few percent from those obtained by using systems as small as consisted of $N = 108$ spheres. The present results are also compared with literature results indicating systematic disagreement with some of them. For this reason, an independent method of direct determination of elastic properties by the free energy differentiation with respect to deformation in the fixed box ensemble (NVT) is also used. Very good agreement is observed for the results of the latter method and the NpT method when they are extrapolated to the infinitely large system limit. Moreover, the results obtained in the present paper fulfill the self-consistency test between the density dependence of the pressure and the bulk modulusmuch better than the literature data mentioned.

1. INTRODUCTION

Recently, a simple method has been proposed, which does not require knowing the reference state before simulations of the elastic properties of studied models [1], Various tests are necessary to check to what extent this method is useful in studies of model systems. In the present paper the method is applied to study the elastic properties of the f.c.c. hard sphere crystal.

The energy of a hard sphere system is infinite when any two spheres overlap and zero otherwise. The hard sphere interaction potential is nonanalytic and can be thought of as a limiting case of anharmonic interactions. In contrast to various analytic potentials, no zero-temperature harmonic approximation can be constructed for this potential. For this reason the hard sphere system is a demanding test model for various theoretical approximations and simulation methods.

The simulations described in the present paper were performed for the defect-free f.c.c. crystal which has been earlier studied in the literature by other methods [2-4]. The main aim of the present paper is to compare the obtained results with results of other methods.

The paper is organized as follows. In Section 2 we give some basic formulae necessary to discuss elasticity of the f.c.c. hard sphere crystal and the NpT simulation method used in this paper. In Section 3 we present some simulation details. In Section 4 results of the NpT

simulations are compared with the literature data [2-4] and with some independent *NVT* simulation runs. The last section (Section 5) contains summary and conclusions.

2. BASIC FORMULAE

Elastic properties of cubic crystals are discussed in detail in the preceding paper [1]. In this chapter the discussion is restricted to some theoretical approximations used in this paper.

2.1. Free volume approximation

It is known [5] that the f.c.c. packing of hard spheres corresponds to the maximum density in this system. Because of the non-analytic character of the hard interactions the properties of the system are singular at the close packing. In the close packing *limit,* however, the asymptotic values of the pressure and elastic constants of hard spheres can be described by the free volume approximation [6, 7]. The free volume (FV) approach consists in observation that at high densities the spheres can be thought of as moving in shells formed by their nearest neighbours [6, 8-10]. The configurational partition function of the system is then approximated by the product of free volumes of all the particles. In the simplest (smoothed) FV approximation, when the free volume available for each particle is approximated by a sphere [8], the free energy per hard sphere can be written as

$$f_{SFV} = -3kT \ln\left(\left(\frac{V}{V_{cp}}\right)^{\frac{1}{3}} - 1\right), \tag{1}$$

where V is the volume and V_{cp} is its close packed limit. This leads to the following equations for the pressure and the bulk modulus:

$$p_{SFV} = \frac{NkT}{V}\frac{1}{1-\left(\frac{V_{cp}}{V}\right)^{\frac{1}{3}}}, \tag{2}$$

$$B_{SFV} = \frac{NkT}{V}\frac{1-\left(\frac{2}{3}\right)\left(\frac{V_{cp}}{V}\right)^{\frac{1}{3}}}{\left(1-\left(\frac{V_{cp}}{V}\right)^{\frac{1}{3}}\right)^2}. \tag{3}$$

Expanding the above equations in the "excess" relative volume, $V/V_{cp} - 1$, and taking into account that $V_{cp} = N\sigma^3/\sqrt{2}$ (where σ is the sphere diameter), one obtains the asymptotic relations for the pressure and bulk modulus [7]

$$p_{FV} = \frac{3\sqrt{2}}{\left(\frac{V}{V_{cp}}\right) - 1} \frac{kT}{\sigma^3}, \tag{4}$$

$$B_{FV} = \frac{3\sqrt{2}}{\left(\left(\frac{V}{V_{cp}}\right) - 1\right)^2} \frac{kT}{\sigma^3}. \tag{5}$$

In the Ref. [7] it has been also conjectured that the asymptotic behaviour of the elastic constants is the same as for B_{FV}

$$C_{ij}^{FV} = \frac{3\sqrt{2}\,A_{ij}}{\left(\left(\frac{V}{V_{cp}}\right) - 1\right)^2} \frac{kT}{\sigma^3}. \tag{6}$$

2. 2. The static limit

The equations obtained from the free volume approximation are expected to contain the relevant information on the asymptotic behaviour of the hard spheres near close packing. One should stress that, at any density below the close packing, the free volume approximation takes into account the particle motions, i.e. it corresponds to the *positive* temperature. *At* the close packing, however, the particles *cannot* move. The information on the influence of the particle motions on the properties of the hard sphere system in the close packing limit can be extracted by considering a static, i.e. *zero temperature,* f.c.c. lattice whose nearest-neighbouring sites (distanced by σ) interact by the potential, $u(r) = (\sigma/r)^n$ in the limit $n \to \infty$. The latter limit can be thought of as the hard-potential *static limit.* The pressure, bulk modulus, the elastic constants, and the Poisson ratio of a static lattice of points interacting by the n-inverse-power potential are the following

$$p^{\text{static}} = 2^{\frac{3}{2}} n\, a^{-(n+3)}, \tag{7}$$

$$B^{\text{static}} = \left(\frac{n}{3} + 1\right) p^{\text{static}}, \tag{8}$$

$$C_{11}^{\text{static}} = \left(\frac{n}{2} + 1\right) p^{\text{static}}, \tag{9}$$

$$C_{12}^{\text{static}} = \frac{1}{2} C_{11}^{\text{static}}, \tag{10}$$

$$C_{44}^{\text{static}} = \frac{1}{2} C_{11}^{\text{static}}, \tag{11}$$

$$\nu^{\text{static}} = \frac{n+6}{3n+6}. \tag{12}$$

Per analogy to (6) one can define the ratios $A_{ij}^{\text{static}} \equiv \lim_{n\to\infty} C_{ij}^{\text{static}}/B^{\text{static}}$ which can be compared with the free volume approximation.

2. 3. The Poisson ratio

An important quantity, characterizing deformations of elastic media is the Poisson ratio, ν [11]. Roughly speaking, it measures the negative ratio of a transverse dimension change to a longitudinal dimension change of a body under longitudinal stress. In general, systems of the cubic symmetry are not isotropic and their Poisson ratio is direction-dependent. For the longitudinal stress acting along one of the crystalline axes the Poisson ratio does not depend on the transverse direction and can be easily expressed by the elastic constants

$$\nu = \frac{B_{12}}{B_{11}+B_{12}} \equiv \frac{C_{12}+p}{C_{11}+C_{12}}. \tag{13}$$

From the equations (4), (6) and from the definition of the Poisson ratio (13) one obtains the following formula in the limit of $V/V_{cp} \to 1$

$$\nu_{cp} = \frac{A_{12}}{A_{11}+A_{12}}. \tag{14}$$

3. THE SIMULATIONS

Most of simulations in this paper were performed in the *NpT* ensemble by a method following the Parrinello-Rahman idea of averaging strain fluctuations [12], which has been further developed in the references [13, 14]. The version of this method applied here, based on [15], was described in detail in [1],

The cubic samples consisted of $N = 4n^3$ spheres. Typical lengths of the runs were equal 3×10^6 trial steps per particle (cycles) for $n = 3$, 5×10^6 cycles for $n = 4$, 10^7 cycles for $n = 5$, 2×10^7 cycles for $n = 6$, and 10^s for $n = 10$, after equilibration. Some longer runs were also performed to check the convergence of the method.

To obtain an independent test of the *NpT* scheme, some calculations were done in the *NVT* ensemble. In the *NVT* simulations the elastic free energy of the system was computed as a function of the deformation (strain). Using the free energy expansion with respect to the strain, the elastic constants C_{ij} were obtained by numerical differentiation of the free energy with respect to the strain. About 20 deformations were used to determine each of the elastic constants C_{11}, C_{12},

C_u. The free energy of each deformation was obtained by 20-point or 40-point Gauss-Legendre integration (with each run consisted, respectively, of either of 2 x 10^5 or of 10^5 cycles after 2 x 10^4 equilibration cycles) along a thermodynamically reversible path joining the hard sphere crystal with the harmonic crystal [16].

4. RESULTS AND DISCUSSION

In Figures 1-3, the simulation data obtained in the present study for $N \to \infty$ are compared with the literature results [2-4], In these figures, the ordinates of the linear fits at close packing characterize quantitatively the singular behaviour of the studied quantities described by (6). The coefficients A_{ij} obtained in this work are collected in Table I.

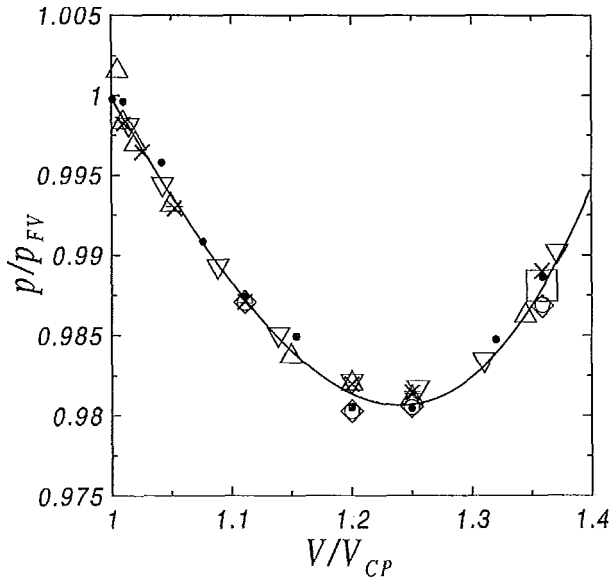

Fig. 1. The equation of state of the f.c.c phase of hard spheres. The pressure is divided by the free volume pressure $p^{(FV)}$. The up-triangles (▵ represent the equation of state data from Ref. [17] and the down-triangles (▽) – the data of Ref. [18]. The meaning of symbols is the following: full dots (•) represent the present *NpT* simulations, open circles (○) – the present *NVT* simulations, diamonds (◇) – the data of Ref. [3], the large squares (□) – the data of Ref. [2], and the crosses (×) – the data of Ref. [4]. The thin continuous line is a polynomial fit to all the presented data

Table I. The extrapolated ratios of the elastic constants to the bulk modulus, A^N_{ij} and the Poisson ratio, ν^c_{pu} in the close packing limit obtained in the presentn work, in the Ref. [4], and in the static limit [see equations (7)-(12)]

u	This work	Ref. [4]	*static*
A_{11}	2.026(18)	2.133(66)	3/2
A_{12}	0.489(18)	0.434(33)	3/4
A_{44}	1.313(8)	1.381(26)	3/4
ν_{cp}	0.194(6)	0.169(12)	1/3

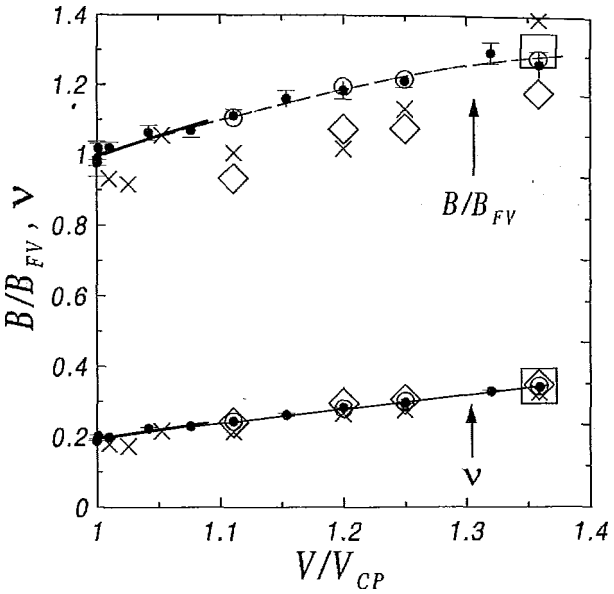

Fig. 2. The Poisson ratio, v, and the bulk modulus, $B = (C_{11} + 2C_{12} + p)/3$, of hard spheres. (The bulk modulus is divided by the free volume bulk modulus $B^{(FV)}$). The meaning of symbols is the same as in Fig. 1. The dashed line for the bulk modulus is obtained by differentiation of the equation of state fit shown in Fig. 1. The thin continuous line for the Poisson ratio is drawn to guide the eyes. The thick continuous lines are linear fits to the points obtained for the five highest pressures

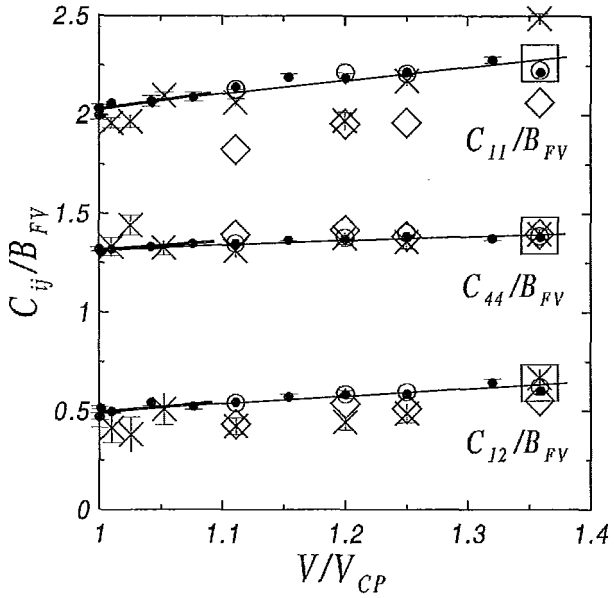

Fig. 3. The elastic constants, C_{ij}, of hard spheres divided by the free volume bulk modulus $B^{(FV)}$. The meaning of symbols is the same as in Fig. 1. The thin continuous lines are drawn to guide the eyes. The thick continuous lines are linear fits to the points obtained for the five highest pressures

It can be seen that the agreement between the *NpT* method used in this paper and the results obtained in the Ref. [2] is excellent for all the presented quantities in the limit $N \to \infty$. A rather good agreement is also seen for the equation of state, the Poisson ratio, and the elastic constant C_{44} determined in the present paper and in the Refs. [3, 4], despite that the Ref. [3] concerns systems not exceeding N - 108 hard spheres. Although a fair agreement is obtained between

the constants C_{11} of the present work and those reported in the Ref. [4], their C_{12} and the bulk modulus seem to be lower than our data. Also the values of C_{11}, C_{12} and the bulk modulus obtained in [3] seem to be systematically lower than the values obtained here. Why it is so, remains an open question.

As not all the literature data show a good agreement with the results of the *NpT* simulations, some *NVT* calculations were performed to supply additional precise and independent information. In Table II a comparison of the *NpT* and *NVT* simulation data is shown for a single phase point. It can be seen that the agreement between both the methods is good in the limit $N \to \infty$. It can be also seen that the results obtained for systems as small as having N- 108 particles differ by only a few (three) percent from the values extrapolated for $N \to \infty$ limit. This indicates that relatively cheap computationally studies of small systems can give reasonable estimates of this limit. Some more results of the *NVT* simulations are shown in Figures 1-3. It can be seen that the *NpT* and the *NVT* results obtained in the present work are in a very good agreement with each other.

Table II. Comparison of the hard sphere elastic constants obtained in the *NpT* simulations with variable box shape and in the *NVT* simulations; $\rho^* = V_{cp}/V$, $p^* = p\sigma^3/kT$, $C_{ij}^* = C_{ij}\sigma^3/kT$

N	p^*	ρ^*	C_{11}^*	C_{12}^*	C_{44}^*
		NpT			
108	37.69	.8991(2)	716(2)	186(2)	454(1)
256	37.69	.8996(1)	729(4)	185(5)	462(2)
500	37.69	.89977(6)	731(3)	190(3)	464(2)
4000	37.69	.89996(5)	733(4)	185(4)	459(2)
∞	37.69	.89997(4)	735(4)	187(4)	462(2)
		NVT			
108	37.34(4)	.9	724(5)	183(4)	461(3)
256	37.53(3)	.9	729(4)	186(3)	463(3)
500	37.64(1)	.9	731(4)	184(3)	464(3)
4000	37.667(3)	.9	732(3)	185(3)	462(3)
∞	37.689(4)	.9	733(3)	185(3)	463(3)

An additional test for the elastic constants computed by different simulation methods bases on the fact that the bulk modulus can be obtained directly from the izotherm of the f.c.c. phase which is known with high accuracy [17, 18]

$$B = -V\frac{\partial p}{\partial V}. \tag{15}$$

On the other side the bulk modulus is a simple combination of the simulated elastic constants

$$B = \frac{\left(B_{11} + 2B_{12}\right)}{3}. \tag{16}$$

Hence, to check the (self-)consistency of various methods used to determine the elastic properties

we decided to compare the simulation results for the equation of state and the bulk modulus. In Figure 1 we show a few fits for the equation of state obtained from various simulations. The bulk modulus dependences on the relative volume obtained from these fits are compared in Figure 2 with the simulation data. It can be seen that the agreement between the hard sphere equation of state and the bulk modulus is excellent for the present data and the Runge-Chester result. This convinces us that the present method gives correct results which are more accurate than some other literature data [3, 4],

5. SUMMARY AND CONCLUSIONS

Elastic properties of the f.c.c. defect-free crystalline structures of hard spheres were determined by *NpT* Monte Carlo simulations based on analysis of the box matrix fluctuations. The *NpT* data were compared with results of independent *NVT* simulations, showing an excellent agreement. Such an agreement was also obtained with results of the Runge-Chester simulations [2]. The results obtained in the present paper and those of Runge and Chester [2] pass very well the self-consistency test between the pressure-density dependence and the bulk modulus dependence on the density. The latter test is fulfilled less satisfactory for some other literature data [3, 4] which show also less satisfactory agreement with the present results.

It follows from the present simulations that the asymptotics of the obtained equation of state, bulk modulus, and elastic constants are in very good agreement with predictions of a simple version of the free volume theory. The coefficients of the leading singularities of elastic constants in the vicinity of the close packing have been determined. These coefficients allow one to calculate the Poisson ratio of hard spheres in the close packing limit. The obtained result is by about 40% lower than the Poisson ratio of the static model. The same conclusion is obtained for various two-dimensional systems [19-23] what indicates that thermal motions can reduce substantially the Poisson ratio near close packing.

It follows from the present study that simulations of systems as small as N - 108 give elastic constants and Poisson ratios which differ by only a few percent from the results obtained by extrapolation to the $N \to \infty$ limit. Simplicity of the used *NpT* method, for which there is no need to compute pressure or its derivatives, and possibility to calculate *all* the elastic constants in a *single* run make the method attractive in situations when quick estimates of the elastic properties are required.

Acknowledgements

We are grateful to Dr. O. Farago for sending us the simulation data used for preparing figures in [4]. One of us (K.W.W.) is grateful to Professor V. Kravtsov for the invitation to visit the Condensed Matter Research Group at the A. Salam International Centre for Theoretical Physics (ICTP) and to members of the Group for hospitality at the ICTP. Part of this work was supported by the grant 4T11F01023 of the Polish Committee for Scientific Research (KBN). Part of the calculations was performed at the Poznań Computer and Networking Center (PCSS).

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