

Fluctuation formalism for elastic constants in hard-spheres-and-tethers systems

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Methods which relate the elastic constants of thermodynamic systems to the fluctuations of the pressure or the volume are called “fluctuation” methods. In this paper we derive expressions, within the fluctuation method, for determining elastic constants in systems composed of hard spheres tethered by inextensible bonds. Such systems are frequently used as athermal models of real physical systems whose thermodynamic properties are primarily determined by entropy rather than energy. Our expressions relate the elastic constants to the probability densities of contacts between the spheres and the probability densities of having stretched bonds. We use our formalism to compute, from Monte Carlo simulations, the elastic constants of hard-sphere systems. Our results agree well with analytical predictions and improve the existing numerical data.

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I. INTRODUCTION

The theory of elasticity describes deformations of thermodynamic systems in response to external forces. When a system is deformed, the distance between two bulk points, which prior to the deformation were separated by \vec{R} , becomes

$$r = [R_i R_j (\delta_{ij} + 2 \eta_{ij})]^{1/2}, \quad (1)$$

where the subscripts denote Cartesian coordinates, and summation over repeated indices is implied. The quantities η_{ij} , which describe the deformation, are the components of the *Lagrangian strain tensor*, while δ_{ij} is the Kröner delta. If Eq. (1) can be applied to any pair of bulk points, i.e., η_{ij} is independent of the position, then the deformation is called *homogeneous*. Usually, however, Eq. (1) can only be applied to neighboring points, i.e., η_{ij} is not constant in the entire volume. In an atomic system it is convenient to apply deformation with constant η_{ij} to all *boundary* points, while the positions of internal atoms are determined by the laws of statistical mechanics. This (constant) η_{ij} is *defined* as the homogeneous strain applied to such a system. The mean free energy density, $f = F/V_0$ (per original, unstrained, unit volume) of a system subjected to a small deformation can be expanded in a power series in the strain variables

$$f(\{\eta\}) = f(\{0\}) + \sigma_{ij} \eta_{ij} + \frac{1}{2} C_{ijkl} \eta_{ij} \eta_{kl} + \dots \quad (2)$$

The coefficients in this expansion are the *stress tensor* σ_{ij} and the *tensor of elastic constants* C_{ijkl} , characterizing the elastic response of a given material.

Condensed matter systems can be broadly divided into two classes: those whose physical properties are determined by energy considerations, and those which are entropy dominated. Hard crystalline materials are examples of materials of the first kind. These systems are likely to be found in their energy ground states, while thermal fluctuations allow only small deviations from these configurations. When such a system is deformed, a macroscopic number of atoms are shifted from their equilibrium positions, and this involves a large

energy penalty. This is the origin of their highly nonflexible nature. Rubber and gels are examples of materials of the second kind. In these systems different microscopic configurations possess very similar internal energies. Energy scales related to translations of atoms and rotations of bonds, in soft materials, are of the order of kT and, therefore, tend to be obscured by thermal fluctuations. Strain, applied to the system, imposes topological restrictions on allowed microscopic configurations, thus leading to a reduction in entropy, which is essentially the (logarithm of the) number of microscopic configurations. The significant response of such systems to a modest shear results from the moderate free energy differences associated with this entropy reduction.

Computational methods for calculation of elastic constants are classified into “strain” methods and “fluctuation” methods. In a strain method calculation [1] one evaluates the elastic constants, which are the derivatives of the stress tensor components with respect to the strain variables, by performing numerical differentiation, i.e., by measuring the (small) stress variations in response to small deformations. In the fluctuation method [2], on the other hand, formal expressions for the elastic constants are derived, relating them to the mean squared thermal fluctuation of the corresponding stress components (or to the volume fluctuations, if the pressure is fixed [3]). These expressions, obtained by differentiating the free energy twice with respect to the strain, can be computed directly from Monte Carlo (MC) or molecular dynamics simulations performed on the unstrained reference system. The fact that simulations are performed in the reference system, with no need to deform the simulation cell, is the major advantage of the fluctuation method over the strain method, which makes it a more efficient and well-controlled technique. Moreover, unlike the strain method, where different deformations must be applied in order to compute the different elastic constants, in the fluctuation method they are all computed in a single run.

In this paper we focus our attention on central force systems, where the internal energy is the sum of pair interactions

$$E = \sum_{\alpha \neq \beta} \phi(r^{\alpha\beta}). \quad (3)$$

[$r^{\alpha\beta}$ is the distance between atoms α and β . The interactions between various pairs of atoms do not have to be (and, in this work, will not be) identical. Thus, we should denote the pair potential as $\phi_{\alpha\beta}(r^{\alpha\beta})$. However, for brevity we will omit the subscripts of the potential and the indices of the argument $r^{\alpha\beta}$ will serve as an indicator of the specific potential.] For such systems, one can apply the fluctuation formalism provided the pair potential $\phi(r)$ is twice differentiable. This requirement is due to the appearance of the second derivative of $\phi(r)$ in the expressions for the elastic constants (which we shall present in Sec. II). Unfortunately, this requirement is not fulfilled in many models of entropy-dominated systems, such as hard sphere systems and tethered surfaces [4]. In this paper we extend the fluctuation formalism to apply to such models.

The paper is organized in the following way: In Sec. II we explain why models like hard spheres and tethered surfaces are frequently used to study entropy-dominated systems. We also introduce the fluctuation method, and discuss why in its standard form it cannot be used to study the elastic constants of such models. In Sec. III we repeat the mathematical derivation of the *general* fluctuation formalism. We discuss our strategy in obtaining the version of the method to the case of hard-spheres-and-tethers systems. The new formalism is presented in Sec. IV, where a short summary of the derivation of the method and the expressions for the stress and elastic constants are given, while a detailed mathematical derivation of the formalism is relegated to the Appendix. We find a relation between the components of the elastic tensor and the probability densities of contact between spheres and probability densities of having stretched bonds. In Sec. V we demonstrate the validity, efficiency, and accuracy of the method by using our formalism in MC simulations of hard sphere systems. We summarize and discuss the results in Sec. VI.

II. HARD POTENTIALS AND THE FLUCTUATION FORMALISM

The specific details of interatomic interactions are quite unimportant in entropy-dominated systems, due to the minor influence of the internal energy on their thermodynamic properties. In real gases, for instance, the pair potential is frequently sharply repulsive at short distances and weakly attractive at longer separations. If the system is either very dilute or very dense, the attractive part of the potential is hardly felt. In polymer physics, the details of interaction between neighboring monomers often become irrelevant provided that the molecules are sufficiently long. Similar considerations apply to gels, in particular close to the gel point. One can therefore use various ways to model these interactions provided they capture the essential physical features such as excluded volume effects and chemical bonding. One possible method of description is a combination of the purely repulsive 6-12 Lennard-Jones potential, sharply increasing for $r < a$ to represent the excluded volume; and an attractive potential, diverging at $r = b$, representing a bond [5]. An example of such a potential is depicted in Fig. 1. An alternative way is to use “hard” potentials which take only two values: zero or infinity. Excluded volume interactions can be described by the hard sphere potential

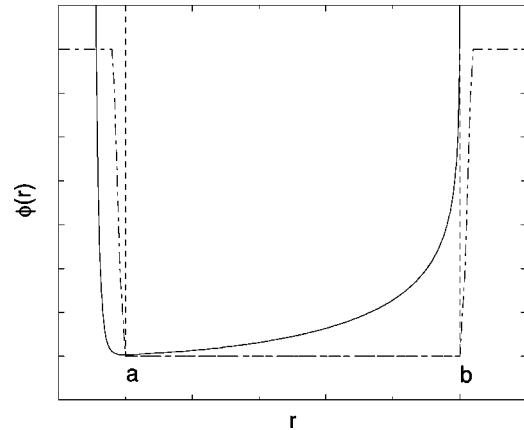


FIG. 1. Three different potentials used to describe the pair interaction between two bonded atoms. The solid line is the potential used in Ref. [5] by Kremer and Grest. The dashed line is the hard-spheres-and-tether potential, $\phi_1(r) + \phi_2(r)$ [Eqs. (4) and (5)]. The dot-dashed line is a smooth approximation to the “hard” potential (see the last paragraph in Sec. III). Both axes are in arbitrary units.

$$\phi_1(r) = \begin{cases} \infty & \text{for } r < a \\ 0 & \text{for } r \geq a. \end{cases} \quad (4)$$

Similarly, real chemical bonds can be replaced by inextensible (“tether”) bonds

$$\phi_2(r) = \begin{cases} 0 & \text{for } r \leq b \\ \infty & \text{for } r > b, \end{cases} \quad (5)$$

which limit the distance between the bonded atoms to b , but have zero energy at all permitted distances. The sum of “hard” potentials (4) and (5), i.e., $\phi_1(r) + \phi_2(r)$, also appears in Fig. 1. The similarity of this potential to the other potential shown in Fig. 1 (as well as to many other “model potentials” used in other works) is evident, and it is therefore not surprising that both of them can be used to study real systems without yielding qualitatively different results.

When real potentials are modeled by their “hard” analogs, the energy of all microscopic configurations is set to the same value—zero (configurations with infinite energy are non-physical). Such models are called *athermal*. Because the internal *configurational* energy is fixed in an athermal system, the Helmholtz free energy is given by $F = -TS$, where S is the entropy and T is the temperature. The physics of athermal systems is exclusively determined by entropy considerations. (Throughout this paper we omit the *kinetic* part of the energy since it is independent of deformation and therefore does not contribute to the elastic behavior. Nevertheless, “kinetic” contributions will appear in the expression for the stress and elastic constants because they will be generated by the configurational part of F .) Entropy itself does not depend on the temperature, but is a function of the geometry of the microscopic structure alone. The temperature dependence of the free energy and other quantities (such as the stress or the elastic constants) is therefore trivially linear. Due to these properties of “hard” potentials, using them can be quite beneficial from mathematical and computational points of view. Simulations of such systems are relatively

simple since there is no need to make any energy calculations, but rather check whether certain geometrical restrictions are obeyed.

Thirty years ago Squire, Holt, and Hoover (SHH) [2] performed MC simulations to evaluate the elastic constants of solid argon. SHH followed the Born theory of elastic constants [6], but applied it to the Helmholtz free energy rather than to the internal energy. As a result, their expression for the elastic constants included a term which was absent from Born's expression. This additional term is equal to the mean squared thermal fluctuation of the stress; hence the name "fluctuation" method. For the present discussion we briefly sketch the SHH derivation originally devised for central force systems. (We repeat it, in detail, in Sec. III.) In such systems the potential internal energy [Eq. (3)] depends only on the relative distances between atoms. Therefore, the La-

grangian strain tensor η_{ij} , which describes the modifications of these distances [Eq. (1)], also describes energy variations and, through the canonical partition function Z , also describes the free energy variations. Once the formal dependence of the free energy on the strain is established, the following expressions for the stress tensor σ_{ij} and the tensor of elastic constants C_{ijkl} (which are the coefficients of the free energy expansion in strain variables [Eq. (2)]) can be easily obtained:

$$\sigma_{ij} = \frac{1}{V} \left. \frac{\partial F}{\partial \eta_{ij}} \right|_{\{\eta\}=\{0\}} = \frac{1}{V} \left\langle \sum_{\langle \alpha\beta \rangle} \phi'(R^{\alpha\beta}) \frac{R_i^{\alpha\beta} R_j^{\alpha\beta}}{R^{\alpha\beta}} \right\rangle - \frac{NkT \delta_{ij}}{V} \quad (6)$$

and

$$\begin{aligned} C_{ijkl} &= \frac{1}{V} \left. \frac{\partial^2 F}{\partial \eta_{ij} \partial \eta_{kl}} \right|_{\{\eta\}=\{0\}} \\ &= \frac{1}{VkT} \left\{ \left\langle \sum_{\langle \alpha\beta \rangle} \phi'(R^{\alpha\beta}) \frac{R_i^{\alpha\beta} R_j^{\alpha\beta}}{R^{\alpha\beta}} \right\rangle \left\langle \sum_{\langle \alpha\beta \rangle} \phi'(R^{\alpha\beta}) \frac{R_k^{\alpha\beta} R_l^{\alpha\beta}}{R^{\alpha\beta}} \right\rangle - \left\langle \left[\sum_{\langle \alpha\beta \rangle} \phi'(R^{\alpha\beta}) \frac{R_i^{\alpha\beta} R_j^{\alpha\beta}}{R^{\alpha\beta}} \right] \left[\sum_{\langle \alpha\beta \rangle} \phi'(R^{\alpha\beta}) \frac{R_k^{\alpha\beta} R_l^{\alpha\beta}}{R^{\alpha\beta}} \right] \right\rangle \right\} \\ &\quad + \frac{1}{V} \left\langle \sum_{\langle \alpha\beta \rangle} \phi''(R^{\alpha\beta}) \frac{R_i^{\alpha\beta} R_j^{\alpha\beta} R_k^{\alpha\beta} R_l^{\alpha\beta}}{(R^{\alpha\beta})^2} \right\rangle - \frac{1}{V} \left\langle \sum_{\langle \alpha\beta \rangle} \phi'(R^{\alpha\beta}) \frac{R_i^{\alpha\beta} R_j^{\alpha\beta} R_k^{\alpha\beta} R_l^{\alpha\beta}}{(R^{\alpha\beta})^3} \right\rangle + \frac{2NkT \delta_{il} \delta_{jk}}{V}. \end{aligned} \quad (7)$$

In the above expressions summation over all distinct pairs of atoms $\langle \alpha\beta \rangle$ is performed. $R^{\alpha\beta}$ is the interparticle distance of the pair under consideration, and $R_i^{\alpha\beta}$ denotes the i th Cartesian component of the vector $\vec{R}^{\alpha\beta} \equiv \vec{R}^\alpha - \vec{R}^\beta$. The symbol $\langle \rangle$ denotes a thermal average. The term in braces in Eq. (7) is the "fluctuation term," while the following two terms form the "Born term." The terms $-NkT \delta_{ij}/V$ and $2NkT \delta_{il} \delta_{jk}/V$ in Eqs. (6) and (7), respectively, are the "kinetic" contributions to the stress and the elastic tensors. They originate in the additive term $-NkT \ln V$ in the free energy.

As mentioned at the end of the Sec. I, the fluctuation formalism cannot be trivially used to measure the elastic constants of systems interacting via "hard" potentials, because these potentials are nondifferentiable while the derivatives of the pair potential are needed in expression (7). In this paper we generalize this expression for the case of "hard" potentials. In fact, the proper expression for the stress tensor in the case of "hard" potentials has been known for many years [7]. It is mathematically simple to derive this expression because the integral that expresses the stress tensor [the averages in Eqs. (6) and (7) are expressed in terms of integrals over the configurations phase space] contains the function $\phi'(r) \exp[-\phi(r)/kT]$, which for "hard" potentials is simply the Dirac δ function. The expression for the tensor of elastic constants includes the functions $\phi'(r)$ and $[\phi'(r)]^2$, which for "hard" potentials yield terms including the derivative and the square of a δ function. The appearance of these functions complicates the mathematical treatment. In

particular, some of the terms in expression (7) diverge when applied for "hard" potentials. We show in the derivation that only the combination of these terms does have a meaningful limit.

III. GENERAL CONSIDERATIONS

If the internal energy of a thermodynamic system is given by Eq. (3), then the corresponding canonical partition function is

$$\begin{aligned} Z &= \frac{(2\pi mkT)^{3N/2}}{h^{3N}} \int_{V(\{\eta\})} \prod_{\gamma=1}^N d\vec{r}^\gamma \exp\left(-\sum_{\langle \alpha\beta \rangle} \phi(r^{\alpha\beta})/kT\right) \\ &= \frac{(2\pi mkT)^{3N/2}}{h^{3N}} Z_C, \end{aligned} \quad (8)$$

where N is the number of atoms, m the mass of an atom, T the temperature, k the Boltzmann constant, and h the Planck constant. The integration volume $V(\{\eta\})$ is the volume in space occupied by the deformed system. The function Z_C is the configurational part of the partition function. The prefactor is associated with the momentum degrees of freedom, and, since they are unaffected by the deformation of the system, it will be omitted hereafter. The (elastic part of the) free energy is related to Z_C by

$$F = -TS = -Tk \ln Z_C. \quad (9)$$

In a canonical ensemble calculation only the surface of the system, not the entire volume, deforms homogeneously. The surface of the system $S(\{\eta\})$ defines the boundaries of the integration volume, $V(\{\eta\})$. The surface $S(\{0\})$ of the strained volume, and the surface $S(\{0\})$ of the unstrained one, are related by a *linear* transformation

$$r_i = M_{ij} R_j, \quad (10)$$

which maps every point \vec{R} on $S(\{0\})$ to its strained spatial position \vec{r} on $S(\{\eta\})$. In Eq. (8) we note that the partition function depends on the strain variables $\{\eta\}$ only through the integration volume $V(\{\eta\})$, and not through the integrand. The idea of the fluctuation formalism is to change the integration variables from r_i to R_i , and replace the strain dependence of the boundaries of integration by strain dependence of the integrand,

$$Z_C = e^{-F/kT} = \int_{V(\{0\})} \prod_{\gamma=1}^N d\vec{R}^\gamma J(\{\eta\}) \times \exp\left(-\sum_{\langle\alpha\beta\rangle} \phi([R_i^{\alpha\beta} R_j^{\alpha\beta} (\delta_{ij} + 2\eta_{ij})]^{1/2})/kT\right), \quad (11)$$

where J is the Jacobian of the linear transformation (10). To find the dependence of J on $\{\eta\}$, we note that the above linear transformation gives

$$|r|^2 = r_k r_k = R_i R_j M_{ik} M_{jk} = R_i R_j M_{ik} M_{kj}^t,$$

where M^t is the transpose of M . When this equation is compared with Eq. (1), we readily see that

$$[MM^t]_{ij} = 2\eta_{ij} + \delta_{ij}.$$

For a system of N particles,

$$J = [\det(M)]^N = \{[\det(M)]^2\}^{N/2} = \{\det(2[\eta] + [I])\}^{N/2}, \quad (12)$$

where $[\eta]$ is the matrix with the elements $[\eta]_{ij} = \eta_{ij}$, and $[I]$ is the identity matrix. With this identity, substituted into Eq. (11), we have a formal expression for the partition function. When Eq. (9) for the free energy is differentiated with respect to $\{\eta\}$, one immediately finds expressions (6) and (7) for the stress and elastic constants.

As we have already explained, the pair potential must be twice differentiable to enable differentiation with respect to $\{\eta\}$. Inserting ‘‘hard’’ potentials directly into the formal expressions for elastic constants leads to what looks like infinite terms or terms involving products of discontinuous functions with δ functions centered at discontinuity, and many other ambiguities and divergences. It is, therefore, convenient to use smooth approximations of these ‘‘hard’’ potentials $\phi_1(r)$ and $\phi_2(r)$ [Eqs. (4) and (5)], for which the averages in expressions (6) and (7) can, in principle, be determined. An example of such a potential, $\phi(r)$, is sketched in Fig. 1. This potential, which resembles the ‘‘hard’’ potential $\phi_1(r) + \phi_2(r)$, has the following features:

- (1) $\phi(r^{\alpha\beta})/kT \ll 1$ for $a + \varepsilon < r < b - \varepsilon$.
- (2) $\phi(r^{\alpha\beta})/kT \gg 1$ for $r < a - \varepsilon$.

(3) If the pair of atoms α and β is tethered, then $\phi(r^{\alpha\beta})/kT \gg 1$ for $r > b + \varepsilon$; otherwise $\phi(r^{\alpha\beta})/kT \ll 1$ for $r > b + \varepsilon$.

(4) In the small intervals $a - \varepsilon < r < a + \varepsilon$ and $b - \varepsilon < r < b + \varepsilon$ between the above regimes, $\phi(r^{\alpha\beta})/kT$ increases (or decreases) sharply. Nevertheless, we assume that along these intervals, $\phi(r)$ is interpolated in a smooth way.

After defining these properties of the potential $\phi(r)$, we substitute it into expressions (6) and (7) for the stress and elastic constants. We then look for what we call the ‘‘athermal limit’’ of these expressions, namely, the limiting expressions obtained when we set the size of the interpolation interval, ε , to zero, while at the same time the potential difference between the regimes $r < a$ and $r > a$ tends to infinity. In the ‘‘athermal limit,’’ $\phi(r)$ becomes a ‘‘hard’’ potential. The ‘‘athermal limit’’ of expressions (6) and (7) can be regarded as the fluctuation expressions of hard-spheres-and-tethers systems. As we show in the derivation, they do not depend on the exact form of approximating potential $\phi(r)$.

IV. STRESS AND ELASTIC CONSTANTS

In this section we introduce our fluctuation expression for the elastic constants of hard-spheres-and-tethers systems. Since the mathematical derivation of the expression is rather lengthy, we will not present it here in detail. We leave the detailed mathematical formulation of the method to the Appendix, while here we restrict ourselves to a short description of the major points in the derivation. We will introduce the expressions obtained for the stress and elastic constants and discuss shortly their ‘‘physical’’ meaning. A demonstration of the applicability of the method is found in Sec. V, where we present numerical results obtained for hard sphere systems, and discuss some technical aspects of the simulations.

Expression (6) for the stress tensor σ_{ij} suggests that the stress is the thermal-volume average of quantities related to the local forces applied to the atoms. For the present discussion, let us assume that we deal with a central force system in which the pair interactions are described by a certain approximating potential $\phi(R)$ (see Sec. III). For such a potential we note that the force $f_{\alpha\beta} = -\phi'(R^{\alpha\beta})$ acting between the pair of atoms $\langle\alpha\beta\rangle$ almost always vanishes, except for very short instances of time (in a statistical ensemble language, only in a small portion of the configurations phase space), when $R^{\alpha\beta} \sim a$, or (if the two atoms are tethered) $R^{\alpha\beta} \sim b$. Hard-spheres-and-tethers models can be regarded as limiting cases in which these pair forces become infinitely large for time intervals which become vanishingly small, keeping the rate of momentum exchange between atoms fixed. From the mathematical point of view it is important to note that what we actually have in the integral expressions for σ_{ij} [Eq. (6)] are the derivatives of the Boltzmann factor, $[\exp(-\phi(R^{\alpha\beta})/kT)]' = [-\phi'(R^{\alpha\beta})/kT] \exp(-\phi(R^{\alpha\beta})/kT)$. In the ‘‘athermal limit’’ the Boltzmann factor converges to a step function where the discontinuity (from zero to unity) occurs at $R^{\alpha\beta} = a$, and an opposite discontinuity (from unity to zero) occurs at $R^{\alpha\beta} = b$, if the pair $\langle\alpha\beta\rangle$ is tethered. The derivative of a step function is just the Dirac δ function. We thus find that, in order to recover the ‘‘athermal limit’’ of σ_{ij} , we only need to perform the simple transformation

$$\phi'(R^{\alpha\beta}) \rightarrow -kT\Delta^{\alpha\beta} \equiv -kT[\delta(R^{\alpha\beta}-a) - \nu^{\alpha\beta}\delta(R^{\alpha\beta}-b)], \quad (13)$$

where $\nu^{\alpha\beta}$, the ‘‘topology variables,’’ take the value 1 if the pair $\langle\alpha\beta\rangle$ is tethered, and 0 otherwise. This gives the known result [7]

$$\sigma_{ij} = -\frac{kT}{V} \left\{ \sum_{\langle\alpha\beta\rangle} \left\langle \frac{R_i^{\alpha\beta} R_j^{\alpha\beta}}{R^{\alpha\beta}} \Delta^{\alpha\beta} \right\rangle + N \delta_{ij} \right\} \quad (14)$$

for the components of the stress tensor. Note that the thermal average of $\Delta^{\alpha\beta}$ is just the difference between the probability density of contact between the pair of spheres $\langle\alpha\beta\rangle$, $p(R^{\alpha\beta}=a+)$, and the probability density, $p(R^{\alpha\beta}=b-)$, of finding the tether connecting them stretched to its maximal length. [If a tether between them does not exist ($\nu^{\alpha\beta}=0$), we simply ignore this second probability density.]

The above transformation [Eq. (13)] is also useful in obtaining the ‘‘athermal limit’’ of many of the terms appearing

in expression (7) for the components of the elastic tensor. More specifically, it should be applied in all the terms which contain the first derivative $\phi'(R^{\alpha\beta})$, or the products $\phi'(R^{\alpha\beta})\phi'(R^{\gamma\delta})$, corresponding to two distinct pairs of atoms $\langle\alpha\beta\rangle \neq \langle\gamma\delta\rangle$. [This product should be simply replaced by $(kT)^2 \Delta^{\alpha\beta} \Delta^{\gamma\delta}$.] This leaves us with only two types of terms, containing the squares of the first derivatives, $\phi'^2(R^{\alpha\beta})$, and the second derivatives, $\phi''(R^{\alpha\beta})$. Finding the ‘‘athermal limit’’ of both terms is the ‘‘missing piece in the puzzle’’ in the formulation of the method. When we substitute an approximating potential into these terms, it is not difficult to find that neither of them has a definite ‘‘athermal limit.’’ Only if we combine them into a single term do we manage to find an appropriate limit, which can be also expressed in terms of the quantities $\Delta^{\alpha\beta}$. A major part of the derivation, which appears in the Appendix, is devoted to the mathematical treatment of this combined term. Here we just give the final expression for the elastic constants:

$$\begin{aligned} C_{ijkl} = & \frac{2NkT}{V} \delta_{il} \delta_{jk} + \frac{kT}{V} \left\{ (D+2) \sum_{\langle\alpha\beta\rangle} \left\langle \frac{R_i^{\alpha\beta} R_j^{\alpha\beta} R_k^{\alpha\beta} R_l^{\alpha\beta}}{(R^{\alpha\beta})^3} \Delta^{\alpha\beta} \right\rangle \right. \\ & - \frac{1}{2} \sum_{\langle\alpha\beta\rangle} \sum_{\gamma \neq \alpha, \beta} \left\langle \left[\frac{R_i^{\alpha\beta} R_j^{\alpha\beta} R_k^{\alpha\beta} R_l^{\alpha\beta}}{(R^{\alpha\beta})^2} \Delta^{\alpha\beta} \left(\frac{\vec{R}^{\alpha\beta} \cdot \vec{R}^{\alpha\gamma}}{R^{\alpha\beta} R^{\alpha\gamma}} \Delta^{\alpha\gamma} + \frac{\vec{R}^{\alpha\beta} \cdot \vec{R}^{\gamma\beta}}{R^{\alpha\beta} R^{\gamma\beta}} \Delta^{\beta\gamma} \right) \right] \right\rangle \\ & + \left[\sum_{\langle\alpha\beta\rangle} \left\langle \frac{R_i^{\alpha\beta} R_j^{\alpha\beta}}{R^{\alpha\beta}} \Delta^{\alpha\beta} \right\rangle \right] \left[\sum_{\langle\alpha\beta\rangle} \left\langle \frac{R_k^{\alpha\beta} R_l^{\alpha\beta}}{R^{\alpha\beta}} \Delta^{\alpha\beta} \right\rangle \right] - \sum_{\langle\alpha\beta\rangle} \sum_{\langle\gamma\delta\rangle \neq \langle\alpha\beta\rangle} \left\langle \frac{R_i^{\alpha\beta} R_j^{\alpha\beta} R_k^{\gamma\delta} R_l^{\gamma\delta}}{R^{\alpha\beta} R^{\gamma\delta}} \Delta^{\alpha\beta} \Delta^{\gamma\delta} \right\rangle \left. \right\}. \quad (15) \end{aligned}$$

In the above expression we distinguish between the different sums: $\sum_{\langle\alpha\beta\rangle}$ denotes summation over all pairs $\langle\alpha\beta\rangle$; $\sum_{\langle\gamma\delta\rangle \neq \langle\alpha\beta\rangle}$ denotes summation over the rest of the pairs, $\langle\gamma\delta\rangle$; while $\sum_{\gamma \neq \alpha, \beta}$ denotes summation over the rest of the atoms, γ (distinct from α and β). D is the dimensionality of the system.

Expressions (14) and (15) relate the stress and elastic constants of hard-spheres-and-tethers systems [in which the pair potential is given by Eqs. (4) and (5)] to the thermal averages of geometrical quantities. We see that except for the kinetic term, originating in the change of the volume of the system caused by the deformation, contributions to the stress are due to pairs of atoms touching each other or due to bonds that are stretched to their maximal length. These are indeed the mechanisms through which tethered hard spheres exchange momentum with each other. Alternatively, expressions (14) and (15) can be understood as follows: In hard-spheres-and-tethers systems entropy measures the extent of configurational phase space. Changes in entropy (to which the stress and elastic constants correspond) are related to the exclusion and inclusion of configurations. When an unstrained configuration is infinitesimally transformed to its deformed correspondent, it may become physically forbidden (or, conversely, physically forbidden configuration may become allowed), only when there exist at least one pair of spheres in contact or when one bond is in maximal stretching. The elas-

tic properties of these systems must, therefore, be related to such events.

V. NUMERICAL EXAMPLES

The major advantage of the fluctuation method is the fact that expressions like Eqs. (14) and (15) provide a direct way for numerical computation of the stress and elastic constants. In order to test the accuracy and efficiency of the method, we have implemented it to measure the elastic constants of hard sphere (HS) systems (i.e., topologies for which $\nu^{\alpha\beta}=0$ for all the pairs $\langle\alpha\beta\rangle$). HS systems have been the subject of an intensive research for several decades now [8]. They serve as the simplest model for real fluids, glasses, and colloids. Moreover, many perturbation theories use them as reference systems for more realistic models including attractive interactions. The phase diagram of HS's is well known. It is a function of one parameter only—the volume fraction, ρ , occupied by the spheres. For $\rho < \rho_{\text{freezing}} = 0.495$ the stable phase is an isotropic fluid phase. At the freezing density an entropically driven first-order phase transition occurs, and over a remarkably large range of densities, $0.495 < \rho < 0.545$, both fluid and solid phases coexist [9]. The solid phase is stable for $\rho > \rho_{\text{melting}} = 0.545$, and can be further compressed up to the close-packing density $\rho_0 = \pi/(3\sqrt{2}) \approx 0.74$ into either the face-centered-cubic (fcc) or the

hexagonal-closed-packed (hcp) crystalline arrangements. The free energy differences between the two structures are extremely small. Recent numerical simulations indicated a preference for the fcc structure [10]. Due to the obvious relation between the phase behavior and the elastic properties of thermodynamic systems, the elasticity of HS systems has also been the subject of many studies (see, e.g., Refs. [11,12]). Nevertheless, the accuracy of the values of the elastic constants still leaves much to be desired. Therefore, although the main purpose of this section is to demonstrate the validity and applicability of the formalism, the numerical results have their own physical usefulness.

The appearance of Dirac δ functions in expressions (14) and (15) deserves a special consideration: In (MC) simulations the average of a certain quantity $g(\vec{R})$ is estimated by

$$\langle g \rangle \approx \frac{1}{N_c} \sum_{p=1}^{N_c} g(\vec{R}_p),$$

where \vec{R}_p is the value of \vec{R} at the p th sampled configuration, and N_c is the total number of MC configurations used in the simulation. Clearly, this sum does not lead to the correct mean when the averaged quantities include δ functions, as we have in expressions (14) and (15), because such quantities vanish at almost every configuration (except for a group of configurations whose measure vanishes—at which their values are not defined at all). This is just a restatement of the fact that in MC simulations we measure probabilities rather than probability densities. A solution to this problem is to measure the relevant quantities every time sphere's separation is found in the small interval of distances $a \leq R \leq a + \epsilon$, and to normalize them by the size of the “bin,” ϵ . If the probability density of pair contact is finite, this approximation would lead to an error which is at most of the order of the small parameter ϵ/a . Obviously, one would like to set the size of ϵ as small as possible, in order to minimize this correction. However, there is a limit to the extent to which ϵ can be reduced, imposed by N_c , the number of MC configurations. As ϵ becomes smaller, one needs more MC samplings in order to count a sufficient number of events at which spheres are separated by a distance inside the bin interval $[a, a + \epsilon]$. An elegant way which incorporates both necessary features, namely, a small ϵ size but also a large number of successful samplings, is to measure a set of independent averages: Each member in this set is the average obtained when we count the contributions of the pairs whose separations fall in one of the intervals

$$\Delta R_n \equiv [a + \epsilon_n - \epsilon/2, a + \epsilon_n + \epsilon/2], \quad n=1, 2, \dots, \quad (16)$$

where $\epsilon_n \equiv (n-1/2)\epsilon$. After evaluating these averages (which are statistically independent quantities since each one is computed using different events), we obtain the correct average by extrapolating them to the limit $\epsilon_n \rightarrow 0$. In Fig. 2 we demonstrate this extrapolation procedure for MC measurements of the pressure and elastic constants of a HS fcc crystal at a reduced density $\rho/\rho_0=0.8$. The curves are the weighted (i.e., each point was weighted by a reciprocal to its error bar) least squares fits of the data to polynomials of the third order in ϵ_n .

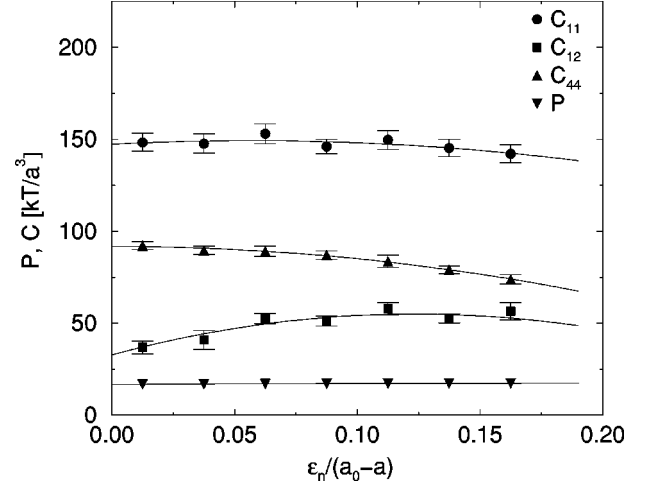


FIG. 2. The pressure P and the three elastic constants C_{11} , C_{12} , and C_{44} for $\rho/\rho_0=0.8$, as a function of ϵ_n [see the definition in Eq. (16)]. ϵ_n was normalized by $a_0 - a$, where a and a_0 are the sphere diameters at ρ and ρ_0 , respectively. The curves are the weighted least squares fits of the third order polynomials in ϵ_n to the data.

Our simulations were performed on systems consisting of 13500 spheres with periodic boundary conditions. We did not use conventional Metropolis single atom steps to generate the MC configurations, but rather collective steps of chains of atoms, as recently suggested by Jaster [13]. We define a MC time unit as the time (measured in number of MC configurations) in which, on the average, we attempt to start one “chain move” from every particle. The acceptance probability of these moves was approximately half. Our simulations were extended over 9×10^5 MC time units. This time is substantially larger than the relaxation time which was estimated from the autocorrelation function of the amplitude of the longest wavelength phonon in the system, and which for all densities [that ranged from the melting density ($\rho/\rho_0=0.736$) up to almost the close packing density ($\rho/\rho_0=0.99$)] was found to be less than 3000 MC time units. The relevant quantities were evaluated every three MC time units. The error estimates, which appear in graphs with the results, represent one standard deviation in the estimates of the corresponding averages.

Due to the cubic symmetry of the fcc lattice, its stress tensor is diagonal, and $\sigma_{xx} = \sigma_{yy} = \sigma_{zz} = -P$, where P is the external pressure applied on the system. The high cubic symmetry also implies that many of the elastic constants are identical. In fact, there are only three independent nonvanishing elastic constants [14], which in the Voigt notation are defined by

$$C_{11} = C_{xxxx} = C_{yyyy} = C_{zzzz},$$

$$C_{12} = C_{xxyy} = C_{yyzz} = C_{zzxx} = \dots,$$

$$C_{44} = C_{xyxy} = C_{yzyz} = C_{zxzx} = \dots.$$

Our results for the pressure P , bulk modulus $\kappa = \frac{1}{3}(C_{11} + 2C_{12} + P)$, and two elastic constants C_{12} and C_{44} of HS fcc solids are presented in Figs. 3–6, respectively (solid circles). Note that since we compute all the non-vanishing components of the tensor C_{ijkl} , we obtain three independent

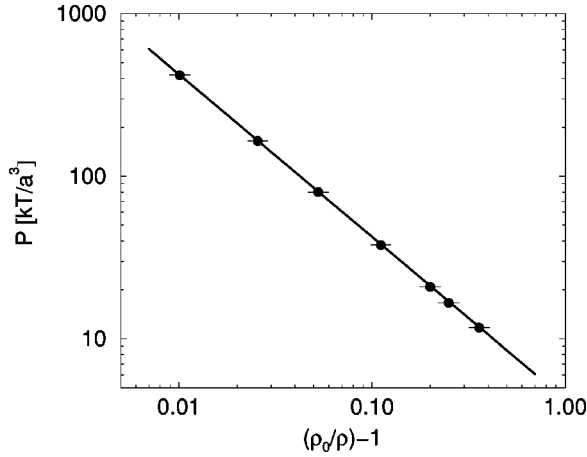


FIG. 3. The pressure P in units of kT/a^3 , as a function of the inverse reduced density, ρ_0/ρ . The circles mark numerical results, while the solid line depicts the free volume approximation for the pressure [Eq. (17)].

estimates for each of the above constants. For instance, $C_{12} \approx C_{xxyy} \approx C_{yyzz} \approx C_{zzxx}$, and therefore we use the estimate $C_{12} = \frac{1}{3}(C_{xxyy} + C_{yyzz} + C_{zzxx})$, which has a smaller statistical error. The solid curves in Figs. 3–6 depict expressions, suggested by Stillinger and Salsburg [15], for the *asymptotic* behavior of these quantities, at the limit of the close packing density, ρ_0 . These authors have shown that the free volume approximation gives the *correct* asymptotic results for the pressure and bulk modulus:

$$P = \frac{3\sqrt{2}}{\rho_0/\rho - 1} \frac{kT}{a^3}, \quad (17)$$

and

$$\kappa = \frac{C_{11} + 2C_{12} + P}{3} = \frac{3\sqrt{2}}{(\rho_0/\rho - 1)^2} \frac{kT}{a^3}. \quad (18)$$

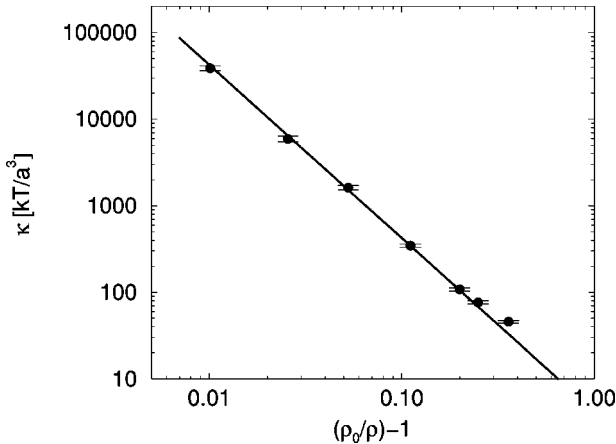


FIG. 4. The bulk modulus κ in units of kT/a^3 , as a function of the inverse reduced density, ρ_0/ρ . The circles mark numerical results, while the solid line depicts the free volume approximation for the bulk modulus [Eq. (18)].

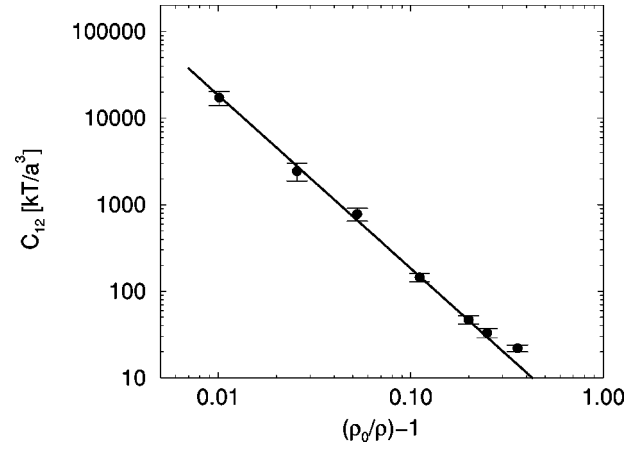


FIG. 5. The elastic constant C_{12} in units of kT/a^3 , as a function of the inverse reduced density, ρ_0/ρ . The circles mark numerical results, while the solid line depicts Eq. (19) with $A_1 = 1.84$.

For the elastic constants C_{12} and C_{44} , it has been conjectured in Ref. [15] that close to ρ_0 their density dependencies have also free volume functional forms:

$$C_{12} = \frac{A_1}{(\rho_0/\rho - 1)^2} \frac{kT}{a^3} \quad (19)$$

and

$$C_{44} = \frac{A_2}{(\rho_0/\rho - 1)^2} \frac{kT}{a^3}, \quad (20)$$

but with constants A_1 and A_2 which have not been accurately determined. Our results confirm the validity of these asymptotic expressions. Most of our data points fall on the solid curves. This shows that the asymptotic expressions provide rather good estimates of the stress and elastic constants, even for densities which are close to the melting density. In Figs. 5 and 6, we used the values $A_1 = 1.84 \pm 0.14$ and $A_2 = 5.86 \pm 0.11$ obtained by fitting the results for the four largest densities ($\rho/\rho_0 = 0.99, 0.975, 0.95,$ and 0.9) to expressions (19) and (20).

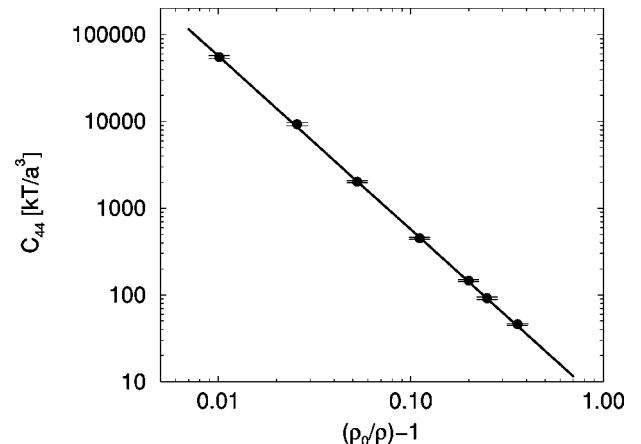


FIG. 6. The elastic constant C_{44} in units of kT/a^3 , as a function of the inverse reduced density, ρ_0/ρ . The circles mark numerical results, while the solid line depicts Eq. (20) with $A_2 = 5.86$.

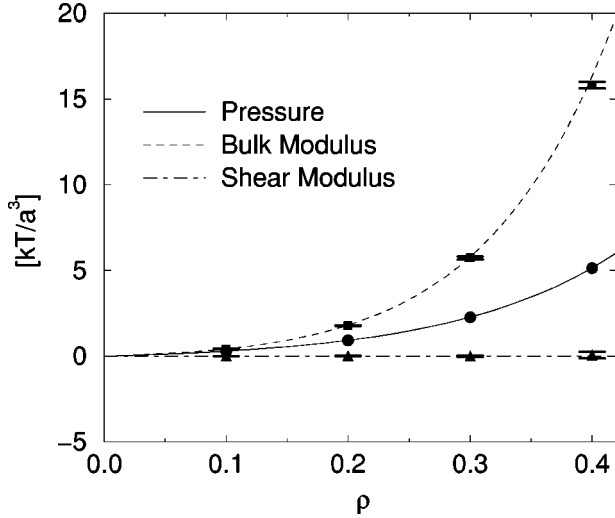


FIG. 7. The pressure and two elastic constants of a HS system in the fluid phase as function of the volume fraction occupied by the spheres, ρ . The shear modulus vanishes at the fluid phase. Curves depicting the pressure and the bulk modulus were calculated using the first seven terms of the virial expansion (see Ref. [16]). The circles, triangles, and squares mark numerical results obtained for densities, $\rho=0.1, 0.2, 0.3$, and 0.4 .

We also compared our results with existing numerical data published by Frenkel and Ladd [11]. They used the strain method technique (see Sec. I) and performed simulations on smaller systems of 108 spheres. At the smaller densities we found their results to be in a very good agreement with ours. At a larger density ($\rho/\rho_0=0.9$), however, we observed a considerable disagreement, where our results seem to be more consistent with the asymptotic expressions of Stillinger and Salsburg. This inconsistency with the results in Ref. [11] is partially explained by finite size effects, but partially it is also due to the difficulties in using the strain method in systems at high pressure. In such systems, small deformations invoke relatively large pressure changes and, therefore, in order to achieve a good estimate for the numerical derivatives one must use extremely small strains and measure the stress components with a very high accuracy. In our high density fluctuation method simulations, we needed to fine tune the small bin size parameter (see earlier in this section). Nevertheless, our results at these densities (which extend beyond the largest density in Ref. [11]) do not suffer from a significant increase of the relative errors, and show excellent agreement with the asymptotic expressions.

Finally, we present results obtained for HS fluid systems (Fig. 7). In the fluid phase the system is isotropic, and therefore characterized by the pressure and two elastic moduli [14]. The shear modulus vanishes, while the pressure and the bulk modulus can be accurately calculated from the virial expansion of the equation of state. (The curves appearing in the figure were derived using the first seven terms of the expansion [16].) We measured the elastic moduli at four different volume fractions $\rho=0.1, 0.2, 0.3$, and 0.4 . The simulations were performed on systems of 8000 spheres over a total time of 1.35×10^6 MC time units. The rest of the technical details are identical to these applied in the solid phase simulations (see text, earlier in this section). The good agreement of the numerical results with the analytical prediction is, again, evident.

VI. SUMMARY AND DISCUSSION

We extended the fluctuation formalism for calculations of the elastic constants, originally devised for conventional potentials, to apply to ‘‘hard’’ potentials. We found expressions relating the components of the tensor of elastic constants to the (two-, three-, and four-point) probability densities of contact between hard spheres and the probability densities of stretching tether bonds, which are the mechanisms through which atoms exchange momentum with each other in such systems. The formalism is not restricted to certain topologies, but is general to all ‘‘hard-spheres-and-tethers’’ systems. In this paper we applied it to HS systems both in fluid and solid phases. Our results, which agree well with analytical predictions, demonstrate the efficiency and accuracy of the method.

Implementing the method in numerical simulations is, generally speaking, quite straightforward. The only non-trivial point is the fact that the probability densities of sphere contacts (and bonds stretching) are evaluated from the probabilities of finding the spheres ‘‘almost touching each other’’ (i.e., finding their separation R in the interval $[a, a + \epsilon]$). Correctly setting the size of ϵ is a key feature for a successful computation. A considerable improvement in the accuracy of the results is obtained by computing several estimates for the probability densities, which are extrapolated to the correct value.

The method presented in this work can be used to study the elastic properties of a wide range of model systems. In a future publication we will present the results of MC simulations of topologically simple regular networks [17]. In the further future, we plan to study more complicated, random, structures.

ACKNOWLEDGMENTS

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APPENDIX: DETAILED DERIVATION OF THE FORMALISM

1. Stress tensor

The starting point of the derivation is the following expression for the stress tensor:

$$\begin{aligned} \sigma_{ij} &= \frac{1}{V} \left. \frac{\partial F}{\partial \eta_{ij}} \right|_{\{\eta\}=0} \\ &= -\frac{kT}{V} \frac{1}{Z_C} \left\{ \int \prod_{\gamma=1}^N d\vec{R}^\gamma \left[\left(\sum_{\langle \alpha\beta \rangle} \frac{-\phi'(R^{\alpha\beta})}{kT} \frac{R_i^{\alpha\beta} R_j^{\alpha\beta}}{R^{\alpha\beta}} \right) \right. \right. \\ &\quad \times \exp \left(- \sum_{\langle \gamma\delta \rangle} \phi(R^{\gamma\delta})/kT \right) \\ &\quad \left. \left. + \frac{\partial J}{\partial \eta_{ij}} \right|_{\{\eta\}=0} \exp \left(- \sum_{\langle \gamma\delta \rangle} \phi(R^{\gamma\delta})/kT \right) \right\}, \quad (A1) \end{aligned}$$

which is easily derived from Eqs. (9) and (11). The first term in the square brackets on the right hand side of Eq. (A1), the

configurational term, is composed of $N(N-1)/2$ terms, each corresponding to one distinct pair. Each of these terms can also be written as

$$\int d\vec{R}^\alpha d\vec{R}^\beta \frac{d[\exp(-\phi(R^{\alpha\beta})/kT)]}{dR^{\alpha\beta}} \left\{ \frac{1}{Z_C} \int \prod_{\gamma \neq \alpha, \beta} d\vec{R}^\gamma \right. \\ \left. \times \left[\exp\left(-\sum_{\langle \gamma\delta \rangle \neq \langle \alpha\beta \rangle} \phi(R^{\gamma\delta})/kT\right) \right] \frac{R_i^{\alpha\beta} R_j^{\alpha\beta}}{R^{\alpha\beta}} \right\}, \quad (\text{A2})$$

where $\sum_{\langle \gamma\delta \rangle \neq \langle \alpha\beta \rangle}$ represents the sum over all pairs $\langle \gamma\delta \rangle$, distinct from the pair $\langle \alpha\beta \rangle$. Note that the limit $\{\eta\} = \{0\}$, was already taken at this stage.

If we now substitute an approximating potential, $\phi(r)$, in the Boltzmann factor, $\exp(-\phi(R^{\alpha\beta})/kT)$, and take the ‘‘athermal limit’’ (see definitions in the last paragraph of Sec. III), we find the Boltzmann factor converging to a step function, where the discontinuity (from zero to unity) occurs at $R^{\alpha\beta} = a$ and an opposite discontinuity (from unity to zero) occurs at $R^{\alpha\beta} = b$ if the pair $\langle \alpha\beta \rangle$ is tethered. The derivative of a step function is just the Dirac δ function. Therefore, in the ‘‘athermal limit,’’ the function $d[\exp(-\phi(R^{\alpha\beta})/kT)]/dR^{\alpha\beta}$, which appears in the integrand in expression (A2), turns into

$$\frac{d[\exp(-\phi(R^{\alpha\beta})/kT)]}{dR^{\alpha\beta}} \rightarrow [\delta(R^{\alpha\beta} - a) - \nu^{\alpha\beta} \delta(R^{\alpha\beta} - b)] \\ \equiv \Delta^{\alpha\beta}, \quad (\text{A3})$$

where $\nu^{\alpha\beta} = 1$ ($\nu^{\alpha\beta} = 0$) for a tethered (nontethered) pair. The remaining part of the integrand,

$$\left\{ \frac{1}{Z_C} \int \prod_{\gamma \neq \alpha, \beta} d\vec{R}^\gamma \left[\exp\left(-\sum_{\langle \gamma\delta \rangle \neq \langle \alpha\beta \rangle} \phi(R^{\gamma\delta})/kT\right) \right] \frac{R_i^{\alpha\beta} R_j^{\alpha\beta}}{R^{\alpha\beta}} \right\} \\ \equiv \tilde{p}(\vec{R}^\alpha, \vec{R}^\beta) \frac{R_i^{\alpha\beta} R_j^{\alpha\beta}}{R^{\alpha\beta}}, \quad (\text{A4})$$

is a smooth function, including at $R^{\alpha\beta} = a$ or $R^{\alpha\beta} = b$. Since only the values of this function at $R^{\alpha\beta} = a$ and (if $\nu^{\alpha\beta} = 1$) $R^{\alpha\beta} = b$ are relevant, the function might be replaced by any other function whose values at these points are the same. For $a < R^{\alpha\beta} < b$, the values of $\tilde{p}(\vec{R}^\alpha, \vec{R}^\beta)$, coincide with the values of the function

$$p(\vec{R}^\alpha, \vec{R}^\beta) = \frac{1}{Z_C} \exp(-\phi(R^{\alpha\beta})/kT) \\ \times \int \prod_{\gamma \neq \alpha, \beta} d\vec{R}^\gamma \exp\left(-\sum_{\langle \gamma\delta \rangle \neq \langle \alpha\beta \rangle} \phi(R^{\gamma\delta})/kT\right),$$

which is the probability density to find atom α in \vec{R}^α and atom β in \vec{R}^β , since in that region $\phi(R^{\alpha\beta}) = 0$. We thus find that, for ‘‘hard’’ potentials, expression (A2) becomes

$$\int d\vec{R}^\alpha d\vec{R}^\beta \left\{ \frac{R_i^{\alpha\beta} R_j^{\alpha\beta}}{R^{\alpha\beta}} \Delta^{\alpha\beta} p(\vec{R}^\alpha, \vec{R}^\beta) \right\} = \left\langle \frac{R_i^{\alpha\beta} R_j^{\alpha\beta}}{R^{\alpha\beta}} \Delta^{\alpha\beta} \right\rangle. \quad (\text{A5})$$

[Unlike the function $\tilde{p}(\vec{R}^\alpha, \vec{R}^\beta)$, the function $p(\vec{R}^\alpha, \vec{R}^\beta)$ suffers a discontinuity at $R^{\alpha\beta} = a$ and (if $\nu^{\alpha\beta} = 1$) $R^{\alpha\beta} = b$, and therefore the transition between the two sides of Eq. (A5) should be made with some caution. The integral in Eq. (A5) and in the following expressions of this type should be understood as if the delta functions reproduce the finite values $p(a+)$ and $p(b-)$. In practice, when we evaluate expression (A5) by a numerical computation, this mathematically delicate point becomes unimportant.] When we sum all $N(N-1)/2$ terms corresponding to all pairs of atoms, we obtain

$$\sigma_{ij}^{\text{conf}} = -\frac{kT}{V} \left\{ \sum_{\langle \alpha\beta \rangle} \left\langle \frac{R_i^{\alpha\beta} R_j^{\alpha\beta}}{R^{\alpha\beta}} \Delta^{\alpha\beta} \right\rangle \right\}. \quad (\text{A6})$$

The second term in Eq. (A1) is known as the kinetic term. It appears even when $\phi \equiv 0$, i.e., for an ideal gas, and it contributes the term $NkT\delta_{ij}/V$. To obtain this contribution we start from Eq. (12), from which we find that

$$\frac{\partial J}{\partial \eta_{ij}} = \frac{N}{2} \{ \det(2[\eta] + [I]) \}^{1/(N/2) - 1} \frac{\partial \{ \det(2[\eta] + [I]) \}}{\partial \eta_{ij}}. \quad (\text{A7})$$

When the explicit expression for $\det(2[\eta] + [I])$ is written down and the derivative with respect to η_{ij} is taken, it is trivial to see that

$$\left. \frac{\partial J}{\partial \eta_{ij}} \right|_{\{\eta\}=0} = N\delta_{ij}, \quad (\text{A8})$$

which when substituted in Eq. (A1) yields

$$\sigma_{ij}^{\text{kinetic}} = -NkT\delta_{ij}/V. \quad (\text{A9})$$

If we now combine Eqs. (A6) and (A9), we obtain expression (14) for the stress tensor:

$$\sigma_{ij} = \sigma_{ij}^{\text{conf}} + \sigma_{ij}^{\text{kinetic}} = -\frac{kT}{V} \left\{ \sum_{\langle \alpha\beta \rangle} \left\langle \frac{R_i^{\alpha\beta} R_j^{\alpha\beta}}{R^{\alpha\beta}} \Delta^{\alpha\beta} \right\rangle + N\delta_{ij} \right\}.$$

2. Tensor of elastic constants

For the tensor elastic constants, we have

$$C_{ijkl} = \left. \frac{\partial^2 F}{\partial \eta_{ij} \partial \eta_{kl}} \right|_{\{\eta\}=\{0\}} \\ = -\frac{kT}{V} \left[\frac{1}{Z_C} \frac{\partial^2 Z_C}{\partial \eta_{ij} \partial \eta_{kl}} - \left(\frac{1}{Z_C} \right)^2 \frac{\partial Z_C}{\partial \eta_{ij}} \frac{\partial Z_C}{\partial \eta_{kl}} \right] \Bigg|_{\{\eta\}=\{0\}}. \quad (\text{A10})$$

If we use Eq. (11), the first of the two terms on the right-hand side of Eq. (A10) splits into four terms (which for the sake of later reference throughout this derivation we denote by T_{1-1} , T_{1-2} , T_{1-3} , and T_{1-4} , respectively)

$$\begin{aligned}
& - \frac{kT}{V} \frac{1}{Z_C} \int \prod_{\gamma=1}^N d\vec{R}^\gamma \left\{ J \frac{\partial^2 \exp\left(\sum_{\langle\alpha\beta\rangle} \phi([R_m^{\alpha\beta} R_n^{\alpha\beta} (\delta_{mn} + 2\eta_{mn})]^{1/2})/kT\right)}{\partial \eta_{ij} \partial \eta_{kl}} \right. \\
& + \frac{\partial J}{\partial \eta_{kl}} \frac{\partial \exp\left(\sum_{\langle\alpha\beta\rangle} \phi([R_m^{\alpha\beta} R_n^{\alpha\beta} (\delta_{mn} + 2\eta_{mn})]^{1/2})/kT\right)}{\partial \eta_{ij}} + \frac{\partial J}{\partial \eta_{ij}} \frac{\partial \exp\left(\sum_{\langle\alpha\beta\rangle} \phi([R_m^{\alpha\beta} R_n^{\alpha\beta} (\delta_{mn} + 2\eta_{mn})]^{1/2})/kT\right)}{\partial \eta_{kl}} \\
& \left. + \frac{\partial^2 J}{\partial \eta_{ij} \partial \eta_{kl}} \exp\left(\sum_{\langle\alpha\beta\rangle} \phi([R_m^{\alpha\beta} R_n^{\alpha\beta} (\delta_{mn} + 2\eta_{mn})]^{1/2})/kT\right) \right\} \Bigg|_{\{\eta\}=0}. \tag{A11}
\end{aligned}$$

The most challenging term in expression (A11) is, of course, the first one, T_{1-1} . If we perform the two derivatives in this term, it yields the following three terms (which we denote by T_{1-1-1} , T_{1-1-2} , and T_{1-1-3} , respectively):

$$\begin{aligned}
& \frac{1}{Z_C} \int \prod_{\gamma=1}^N d\vec{R}^\gamma \left\{ \frac{1}{kT} \exp\left(-\sum_{\langle\gamma\delta\rangle} \phi(R^{\gamma\delta})/kT\right) \left[\sum_{\langle\alpha\beta\rangle} \frac{\phi'(R^{\alpha\beta})}{(R^{\alpha\beta})^3} R_i^{\alpha\beta} R_j^{\alpha\beta} R_k^{\alpha\beta} R_l^{\alpha\beta} \right] - \frac{1}{kT} \exp\left(-\sum_{\langle\gamma\delta\rangle} \phi(R^{\gamma\delta})/kT\right) \right. \\
& \times \left[\sum_{\langle\alpha\beta\rangle} \frac{\phi''(R^{\alpha\beta})}{(R^{\alpha\beta})^2} R_i^{\alpha\beta} R_j^{\alpha\beta} R_k^{\alpha\beta} R_l^{\alpha\beta} \right] + \left. \left(\frac{1}{kT}\right)^2 \exp\left(-\sum_{\langle\gamma\delta\rangle} \phi(R^{\gamma\delta})/kT\right) \left[\sum_{\langle\alpha\beta\rangle} \frac{\phi'(R^{\alpha\beta})}{R^{\alpha\beta}} R_i^{\alpha\beta} R_j^{\alpha\beta} \right] \left[\sum_{\langle\alpha\beta\rangle} \frac{\phi'(R^{\alpha\beta})}{R^{\alpha\beta}} R_k^{\alpha\beta} R_l^{\alpha\beta} \right] \right\}. \tag{A12}
\end{aligned}$$

[Note that in Eq. (A12) the limit $\{\eta\}=\{0\}$, at which $J=1$, was already taken]. Following the derivation of the configurational stress tensor [Eq. (A5)], it can be easily shown that in the ‘‘athermal limit,’’ the term T_{1-1-1} becomes

$$- \sum_{\langle\alpha\beta\rangle} \left\langle \frac{R_i^{\alpha\beta} R_j^{\alpha\beta} R_k^{\alpha\beta} R_l^{\alpha\beta}}{(R^{\alpha\beta})^3} \Delta^{\alpha\beta} \right\rangle. \tag{A13}$$

A straightforward generalization of this derivation shows that the *nondiagonal* elements in term T_{1-1-3} , i.e., those terms for which $\langle\alpha\beta\rangle$ pairs are different in the last two sums, give

$$\sum_{\langle\alpha\beta\rangle} \sum_{\langle\gamma\delta\rangle \neq \langle\alpha\beta\rangle} \left\langle \frac{R_i^{\alpha\beta} R_j^{\alpha\beta} R_k^{\gamma\delta} R_l^{\gamma\delta}}{R^{\alpha\beta} R^{\gamma\delta}} \Delta^{\alpha\beta} \Delta^{\gamma\delta} \right\rangle. \tag{A14}$$

Note that the nondiagonal terms include both three-particle terms [$\langle\alpha\beta\rangle$ and $\langle\alpha\gamma\rangle$] and four-particle terms [$\langle\alpha\beta\rangle$ and $\langle\gamma\delta\rangle$].

We were thus left with the T_{1-1-2} term, and with the *diagonal* elements of the T_{1-1-3} term, which may be written in the following combined form:

$$- \frac{1}{kT} \int \prod_{\gamma=1}^N d\vec{R}^\gamma \left\{ \exp\left(-\sum_{\langle\gamma\delta\rangle} \phi(R^{\gamma\delta})/kT\right) \sum_{\langle\alpha\beta\rangle} \left[\left(\phi''(R^{\alpha\beta}) - \phi'(R^{\alpha\beta})^2/kT \right) \left(\frac{R_i^{\alpha\beta} R_j^{\alpha\beta} R_k^{\alpha\beta} R_l^{\alpha\beta}}{(R^{\alpha\beta})^2} \right) \right] \right\}.$$

Let us now look at one of these expressions, corresponding to the pair $\langle\alpha\beta\rangle$. After performing the integrations over the rest of the coordinates, $\{\vec{R}^\gamma | \gamma \neq \alpha, \beta\}$, we are left with

$$\int d\vec{R}^\alpha d\vec{R}^\beta \tilde{p}(\vec{R}^\alpha, \vec{R}^\beta) \frac{R_i^{\alpha\beta} R_j^{\alpha\beta} R_k^{\alpha\beta} R_l^{\alpha\beta}}{(R^{\alpha\beta})^2} \frac{d^2[\exp(-\phi(R^{\alpha\beta})/kT)]}{d(R^{\alpha\beta})^2} \tag{A15}$$

[$\tilde{p}(\vec{R}^\alpha, \vec{R}^\beta)$ is defined in Eq. (A4)]. At this point we change the variables of integration from $d\vec{R}^\alpha d\vec{R}^\beta$ to $d\vec{R}^{\alpha\beta} d\vec{R}^\beta$, where $\vec{R}^{\alpha\beta} = \vec{R}^\alpha - \vec{R}^\beta$, and then change $d\vec{R}^{\alpha\beta}$ to spherical coordinates $(R^{\alpha\beta})^{D-1} dR^{\alpha\beta} d\Omega^{\alpha\beta}$, where $\Omega^{\alpha\beta}$ is the solid angle aperture around $\vec{R}^{\alpha\beta}$, and D is the dimensionality of the system. We also note that the terms $(R_i^{\alpha\beta} R_j^{\alpha\beta} R_k^{\alpha\beta} R_l^{\alpha\beta})/(R^{\alpha\beta})^2$ in Eq. (A15) can be written as $(R^{\alpha\beta})^2 f_{ijkl}(\Omega^{\alpha\beta})$, where f_{ijkl} is a function of the solid angle alone (for instance, for a two-dimensional system, $f_{xxxx} = \cos^4 \Omega$, $f_{yyyy} = \sin^4 \Omega$, $f_{xyxy} = f_{yxxy} = f_{xyyx} = f_{yyxx} = \cos^2 \Omega \sin^2 \Omega$, etc.). Thus Eq. (A15) takes the form

$$\int d\vec{R}^\alpha d\Omega^{\alpha\beta} dR^{\alpha\beta} \left\{ (R^{\alpha\beta})^{D+1} \tilde{p}(\vec{R}^\alpha, \vec{R}^\beta) f_{ijkl}(\Omega^{\alpha\beta}) \frac{d^2[\exp(-\phi(R^{\alpha\beta})/kT)]}{d(R^{\alpha\beta})^2} \right\}.$$

When integration by parts is performed over the variable $R^{\alpha\beta}$, this expression becomes

$$\begin{aligned}
&= - \int d\vec{R}^\alpha d\Omega^{\alpha\beta} f_{ijkl}(\Omega^{\alpha\beta}) dR^{\alpha\beta} \frac{\partial[(R^{\alpha\beta})^{D+1} \tilde{p}(\vec{R}^\alpha, \vec{R}^\beta)]}{\partial R^{\alpha\beta}} \frac{d[\exp(-\phi(R^{\alpha\beta})/kT)]}{dR^{\alpha\beta}} \\
&= - \int d\vec{R}^\alpha d\Omega^{\alpha\beta} f_{ijkl}(\Omega^{\alpha\beta}) dR^{\alpha\beta} \frac{\partial[(R^{\alpha\beta})^{D+1} \tilde{p}(\vec{R}^\alpha, \vec{R}^\beta)]}{\partial R^{\alpha\beta}} \Delta^{\alpha\beta}. \tag{A16}
\end{aligned}$$

(Integration is taken from 0 to ∞ and, therefore, the boundary terms vanish.) The second expression in Eq. (A16) is obtained for the ‘‘athermal limit’’ using substitution (A3). In order to bring this expression into a more useful form, we perform the derivative in Eq. (A16):

$$\begin{aligned}
&\frac{\partial[(R^{\alpha\beta})^{D+1} \tilde{p}(\vec{R}^\alpha, R^{\alpha\beta}, \Omega^{\alpha\beta})]}{\partial R^{\alpha\beta}} \\
&= (D+1)(R^{\alpha\beta})^D \tilde{p}(\vec{R}^\alpha, R^{\alpha\beta}, \Omega^{\alpha\beta}) \\
&\quad + (R^{\alpha\beta})^{D+1} \frac{\partial[\tilde{p}(\vec{R}^\alpha, R^{\alpha\beta}, \Omega^{\alpha\beta})]}{\partial R^{\alpha\beta}}. \tag{A17}
\end{aligned}$$

After the first term on the right-hand side of Eq. (A17) is substituted into Eq. (A16), we may switch back to the original integration variables, $d\vec{R}^\alpha d\vec{R}^\beta$, and, again, use substitution (A3). In fact, we obtain an expression which is identical with expression (A13), except for a prefactor $(D+1)$. Thus their joint contribution is

$$-(D+2) \sum_{\langle \alpha\beta \rangle} \left\langle \frac{R_i^{\alpha\beta} R_j^{\alpha\beta} R_k^{\alpha\beta} R_l^{\alpha\beta}}{(R^{\alpha\beta})^3} \Delta^{\alpha\beta} \right\rangle. \tag{A18}$$

The task imposed by the second term in Eq. (A17) is slightly more complicated: we need to evaluate $\partial[\tilde{p}(\vec{R}^\alpha, \vec{R}^\beta)]/\partial R^{\alpha\beta}$. We remind the reader that $\tilde{p}(\vec{R}^\alpha, \vec{R}^\beta)$ is given by Eq. (A4). The dependence of \tilde{p} on $R^{\alpha\beta}$ in this expression comes from the exponent

$$\sum_{\langle \gamma\delta \rangle \neq \langle \alpha\beta \rangle} \phi(R^{\gamma\delta}) \tag{A19}$$

appearing in Eq. (A4). Instead of the set of variables $\{\vec{R}^\gamma | \gamma = 1, \dots, N\}$, we may use the set of *independent* variables $\{\vec{R}^\alpha, \vec{R}^\gamma - \vec{R}^\alpha = \vec{R}^{\gamma\alpha} | \gamma = 1, \dots, N, \gamma \neq \alpha\}$, to express the terms in exponent (A19). Since we look for the derivative of $\tilde{p}(\vec{R}^\alpha, \vec{R}^\beta)$ with respect to $R^{\alpha\beta}$ (the size of one of the variables, $\vec{R}^{\beta\alpha}$), we need to find which of the terms in expression (A19) actually depend on this variable. One can easily find that the terms included in the set $\{\phi(R^{\beta\gamma}) | \gamma = 1, \dots, N; \gamma \neq \alpha, \beta\}$ are the relevant terms. $\vec{R}^{\beta\gamma}$ and $\vec{R}^{\alpha\beta}$ are two of the edges of a triangle whose vertices are the positions of atoms α , β , and γ . It is not difficult to show that if the length of $\vec{R}^{\alpha\beta}$ is slightly changed, while the length of $\vec{R}^{\alpha\gamma}$ is fixed, then the change in the length of the third edge, $\vec{R}^{\beta\gamma}$, obeys

$$\frac{\partial R^{\beta\gamma}}{\partial R^{\alpha\beta}} = \frac{\vec{R}^{\alpha\beta} \cdot \vec{R}^{\gamma\beta}}{R^{\alpha\beta} R^{\gamma\beta}}.$$

With this identity, we find in a straightforward manner that

$$\begin{aligned}
\frac{\partial[\tilde{p}(\vec{R}^\alpha, R^{\alpha\beta}, \Omega^{\alpha\beta})]}{\partial R^{\alpha\beta}} &= \tilde{p}(\vec{R}^\alpha, R^{\alpha\beta}, \Omega^{\alpha\beta}) \sum_{\gamma \neq \alpha, \beta} \\
&\quad - \frac{1}{kT} \phi'(R^{\beta\gamma}) \frac{\vec{R}^{\alpha\beta} \cdot \vec{R}^{\gamma\beta}}{R^{\alpha\beta} R^{\gamma\beta}}.
\end{aligned}$$

In this expression the indices α and β appear in an asymmetrical way. If we interchange their roles, we obtain the following symmetrical form:

$$\begin{aligned}
\frac{\partial[\tilde{p}(\vec{R}^\alpha, R^{\alpha\beta}, \Omega^{\alpha\beta})]}{\partial R^{\alpha\beta}} &= \frac{\tilde{p}(\vec{R}^\alpha, R^{\alpha\beta}, \Omega^{\alpha\beta})}{-2kT} \\
&\quad \times \sum_{\gamma \neq \alpha, \beta} \left\{ \phi'(R^{\beta\gamma}) \frac{\vec{R}^{\alpha\beta} \cdot \vec{R}^{\gamma\beta}}{R^{\alpha\beta} R^{\gamma\beta}} \right. \\
&\quad \left. + \phi'(R^{\alpha\gamma}) \frac{\vec{R}^{\alpha\beta} \cdot \vec{R}^{\alpha\gamma}}{R^{\alpha\beta} R^{\alpha\gamma}} \right\}. \tag{A20}
\end{aligned}$$

We now need to substitute this last identity into the integrand of Eq. (A16), switch back to the original integration variables, $d\vec{R}^\alpha d\vec{R}^\beta$, and use transformation (A3), to finally obtain that the contribution of the second term in Eq. (A17) is

$$\begin{aligned}
&-\frac{1}{2} \sum_{\langle \alpha\beta \rangle} \sum_{\gamma \neq \alpha, \beta} \left\{ \left\langle \frac{R_i^{\alpha\beta} R_j^{\alpha\beta} R_k^{\alpha\beta} R_l^{\alpha\beta}}{(R^{\alpha\beta})^2} \Delta^{\alpha\beta} \right. \right. \\
&\quad \left. \left. \times \left(\frac{\vec{R}^{\alpha\beta} \cdot \vec{R}^{\alpha\gamma}}{R^{\alpha\beta} R^{\alpha\gamma}} \Delta^{\alpha\gamma} + \frac{\vec{R}^{\alpha\beta} \cdot \vec{R}^{\gamma\beta}}{R^{\alpha\beta} R^{\gamma\beta}} \Delta^{\beta\gamma} \right) \right\rangle \right\}. \tag{A21}
\end{aligned}$$

We still need to treat terms T_{1-2} , T_{1-3} , and T_{1-4} in Eq. (A11), and the second term in Eq. (A10). Term T_{1-2} is identical to the configurational stress term, except for the multiplicative term $\partial J/\partial \eta_{kl}$ which appears in the former. Therefore, using result (A8), we find that the contribution of this term is

$$N \delta_{kl} \sigma_{ij}^{\text{conf}}. \tag{A22}$$

Similarly, the T_{1-3} term yields

$$N \delta_{ij} \sigma_{kl}^{\text{conf}}. \tag{A23}$$

The second term in Eq. (A10) is obviously equal to

$$\frac{kT}{V} \left\{ \sum_{\langle \alpha\beta \rangle} \left\langle \frac{R_i^{\alpha\beta} R_j^{\alpha\beta}}{R^{\alpha\beta}} \Delta^{\alpha\beta} \right\rangle + N \delta_{ij} \right\} \times \left\{ \sum_{\langle \alpha\beta \rangle} \left\langle \frac{R_k^{\alpha\beta} R_l^{\alpha\beta}}{R^{\alpha\beta}} \Delta^{\alpha\beta} \right\rangle + N \delta_{kl} \right\}. \quad (\text{A24})$$

Finally we need to differentiate expression (A7) with respect to η_{kl} , in order to calculate term T_{1-4} , which is given by

$$-\frac{kT}{V} \frac{\partial^2 J}{\partial \eta_{ij} \partial \eta_{kl}} \Big|_{\{\eta\}=\{0\}} = -\frac{kT}{V} \{N^2 \delta_{ij} \delta_{kl} - 2N \delta_{il} \delta_{jk}\}. \quad (\text{A25})$$

We thus find that the *joint* contribution of these four terms Eqs. [(A22)–(A25)] to the expression for the tensor of elastic constants is

$$\frac{2NkT}{V} \delta_{il} \delta_{jk} + \frac{kT}{V} \left\{ \sum_{\langle \alpha\beta \rangle} \left\langle \frac{R_i^{\alpha\beta} R_j^{\alpha\beta}}{R^{\alpha\beta}} \Delta^{\alpha\beta} \right\rangle \right\} \times \left\{ \sum_{\langle \alpha\beta \rangle} \left\langle \frac{R_k^{\alpha\beta} R_l^{\alpha\beta}}{R^{\alpha\beta}} \Delta^{\alpha\beta} \right\rangle \right\}. \quad (\text{A26})$$

To this contribution we need to add terms (A14), (A18), and (A21) to obtain the following final expression for the tensor of elastic constants (15):

$$C_{ijkl} = \frac{2NkT}{V} \delta_{il} \delta_{jk} + \frac{kT}{V} \left\{ (D+2) \sum_{\langle \alpha\beta \rangle} \left\langle \frac{R_i^{\alpha\beta} R_j^{\alpha\beta} R_k^{\alpha\beta} R_l^{\alpha\beta}}{(R^{\alpha\beta})^3} \Delta^{\alpha\beta} \right\rangle - \frac{1}{2} \sum_{\langle \alpha\beta \rangle} \sum_{\gamma \neq \alpha, \beta} \left\langle \left[\frac{R_i^{\alpha\beta} R_j^{\alpha\beta} R_k^{\alpha\beta} R_l^{\alpha\beta}}{(R^{\alpha\beta})^2} \Delta^{\alpha\beta} \right. \right. \right. \\ \left. \left. \times \left(\frac{\vec{R}^{\alpha\beta} \cdot \vec{R}^{\alpha\gamma}}{R^{\alpha\beta} R^{\alpha\gamma}} \Delta^{\alpha\gamma} + \frac{\vec{R}^{\alpha\beta} \cdot \vec{R}^{\beta\gamma}}{R^{\alpha\beta} R^{\beta\gamma}} \Delta^{\beta\gamma} \right) \right] \right\rangle \\ \left. + \left[\sum_{\langle \alpha\beta \rangle} \left\langle \frac{R_i^{\alpha\beta} R_j^{\alpha\beta}}{R^{\alpha\beta}} \Delta^{\alpha\beta} \right\rangle \right] \left[\sum_{\langle \alpha\beta \rangle} \left\langle \frac{R_k^{\alpha\beta} R_l^{\alpha\beta}}{R^{\alpha\beta}} \Delta^{\alpha\beta} \right\rangle \right] - \sum_{\langle \alpha\beta \rangle} \sum_{\langle \gamma\delta \rangle \neq \langle \alpha\beta \rangle} \left\langle \frac{R_i^{\alpha\beta} R_j^{\alpha\beta} R_k^{\gamma\delta} R_l^{\gamma\delta}}{R^{\alpha\beta} R^{\gamma\delta}} \Delta^{\alpha\beta} \Delta^{\gamma\delta} \right\rangle \right\}.$$

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- [1] R. G. Treloar, Rep. Prog. Phys. **36**, 755 (1973); R. Everears, K. Kremer, and G. S. Grest, Macromol. Symp. **93**, 53 (1995).
[2] D. R. Squire, A. C. Holt, and W. G. Hoover, Physica (Amsterdam) **42**, 388 (1969).
[3] M. Parrinello and A. Rahman, J. Chem. Phys. **76**, 2662 (1982).
[4] Y. Kantor, M. Kardar, and D. R. Nelson, Phys. Rev. Lett. **57**, 791 (1986); Phys. Rev. A **35**, 3056 (1987).
[5] K. Kremer and S. G. Grest, J. Chem. Phys. **92**, 5057 (1990); **94**, 4103 (1991).
[6] M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Oxford University Press, Oxford, 1954), pp. 129–154.
[7] J. A. Barker and D. Henderson, Mol. Phys. **21**, 187 (1971).
[8] For a recent review article on hard spheres, see A. P. Gast and W. B. Russel, Phys. Today **51**(12), 24 (1998), and references therein.
[9] W. G. Hoover and F. H. Ree, J. Chem. Phys. **49**, 3609 (1968); B. J. Alder, W. G. Hoover, and D. A. Young, *ibid.* **49**, 3688 (1968).
[10] A. D. Bruce, N. B. Wilding, and G. J. Ackland, Phys. Rev. Lett. **79**, 3002 (1997); S. Pronk and D. Frenkel, J. Chem. Phys. **110**, 4589 (1999).
[11] D. Frenkel and A. J. C. Ladd, Phys. Rev. Lett. **59**, 1169 (1987).
[12] B. B. Laird, J. Chem. Phys. **97**, 2699 (1992).
[13] A. Jaster, Physica A **264**, 134 (1999).
[14] D. C. Wallace, in *Solid State Physics*, edited by H. Ehrenreich, F. Seitz, and D. Turnbull (Academic, New York, 1970), Vol. 25, p. 301.
[15] F. H. Stillinger, Jr. and Z. W. Salsburg, J. Chem. Phys. **46**, 3962 (1967).
[16] M. Luban and J. P. J. Michels, Phys. Rev. A **41**, 6796 (1990).
[17] O. Farago and Y. Kantor (unpublished).