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Quick and accurate estimation of the elastic constants using the minimum image method

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ABSTRACT

A method for determining the elastic properties using the minimum image method (MIM) is proposed and tested on a model system of particles interacting by the Lennard-Jones (LJ) potential. The elastic constants of the LJ system are determined in the thermodynamic limit, $N \to \infty$, using the Monte Carlo (MC) method in the NVT and NPT ensembles. The simulation results show that when determining the elastic constants, the contribution of long-range interactions cannot be ignored, because that would lead to erroneous results. In addition, the simulations have revealed that the inclusion of further interactions of each particle with all its minimum image neighbors even in case of small systems leads to results which are very close to the values of elastic constants in the thermodynamic limit. This enables one for a quick and accurate estimation of the elastic constants using very small samples.

1. Introduction

Knowledge of elastic properties of materials around us is important not only from the scientific point of view but also for practical applications. In solids, the elastic properties can be described by the elastic constants which determine the relationship between strain and stress. Research on the elastic constants is carried out at different levels from microscopic to macroscopic, using both the theoretical and experimental methods. A special place in the study of elastic properties is taken by computer simulations, which can relatively easy supply data in areas where the experiments are either difficult or even cannot be performed, e.g. at extreme temperatures or pressures, or can be used to analyze hypothetical models or materials with unusual properties. The pioneering simulation work by Squire, Holt, and Hoover [1] was related to Monte Carlo calculations of the elastic properties of solid argon using the Lennard-Jones interatomic pair potential:

$$\phi(r_{ij}) = 4\epsilon\left[\left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^{6}\right], \tag{1}$$

where σ is the particle diameter, ϵ sets the energy scale, and $\mathbf{r}_{ij}$ is the distance between particles i and j. Since that time a number of simulation methods to calculate the elastic properties of atomic systems were established [2–11]. In the current work a simple extension for basic methods of calculation of elastic constants is proposed and tested on Lennard-Jones system.

The LJ potential plays a significant role in the computer simulations, not only because of its simplicity and elegance, but mainly for the fact that it is a model potential which allows to describe some physical properties of noble gases and various properties of simple liquids [12]. It is also a reference potential used to test variety of new theories and computational methods [13]. Typically, new methods to calculate the elastic constants are tested on the system of particles interacting via LJ potential only between nearest neighbors [14,3,15,16,6,17,8,9] so called a nearest-neighbor Lennard-Jones (LJnn) potential. From the point of view of conducting simulation, it is a well defined and very comfortable model, because a researcher does not have to take into account the long-range interactions. However, in real systems one can rarely afford such a simplification. There are few works devoted to the calculations of elastic properties of the LJ system including the further neighborhood [1,18,19], because such simulations are much more time consuming than those taking into account only the nearest neighbors or those with some fixed length of truncation of the LJ potential. Many different simplifications of the LJ potential can be found in the literature, starting from the aforementioned LJnn model, by the systems, wherein the particles interact with some cut potential [20] until a cut and sifted potential [21]. The last one has the advantage in molecular dynamics (MD) simulations that there is no discontinuity in the potential or the force. It is not surprising that the system in each of these approximations will have different thermodynamic properties.

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An accounting of the long-range interactions in computer simulations is usually quite expensive. For example, when considering the interactions of ions or dipoles one cannot avoid either counting the Ewald sum [22–24], or applying the particle–mesh method [25] or application of the method of minimal image [26,27]. However, to obtain correct results for the energy and pressure in the case of the LJ potential system, the long-range corrections are often used. The long-range or tail corrections are computed by following formulas:

$$U^*_{LRC} = \frac{8}{9}\pi\rho^*\left[\left(\frac{\sigma}{r_c}\right)^9 - 3\left(\frac{\sigma}{r_c}\right)^3\right], \tag{2}$$

$$p^*_{LRC} = \frac{32}{9}\pi\rho^{*2}\left[\left(\frac{\sigma}{r_c}\right)^9 - \frac{3}{2}\left(\frac{\sigma}{r_c}\right)^3\right], \tag{3}$$

where $U^* = U/\epsilon$ is the dimensionless energy, $p^* = p\sigma^3/\epsilon$ is the dimensionless pressure, r_c is the cutoff radius of the LJ potential, $\rho^* = (N/V)\sigma^3$ is the reduced density, N is the number of particles, and V is the volume of the system. In the case of the elastic constants the use of analogous corrections does not lead to correct results. So, the effect of long-range interactions cannot be neglected.

The aim of this work is twofold. First, a simple, efficient and fairly accurate method of determining the elastic properties is introduced, which correctly takes into account the long-range interactions. This method, using the convention of minimum images, has been tested in NVT and NPT ensembles. Second, the elastic constants of the system of particles interacting via LJ potential are determined in the limit $N \to \infty$.

2. Elastic constants and basic methods of their calculations

The elastic constants at a fixed temperature are defined as follows:

$$C_{\alpha\beta\gamma\tau} = \frac{1}{V}\left(\frac{\partial^2 F}{\partial\eta_{\alpha\beta}\partial\eta_{\gamma\tau}}\right)_{\eta=0}, \tag{4}$$

where F is the Helmholtz free energy, V is the volume of reference state, η is the strain tensor. In general, taking into account the symmetry of the strain tensor, the tensor of elastic moduli has 21 independent components [28], however, the crystal symmetry usually implies a significant reduction of their number. The face-centered cubic structure (only the crystal with such structure will be considered in this paper) has only three independent elastic constants, which – using the Voigt notation – can be written as follows: $C_{1111} = C_{11}$, $C_{1122} = C_{12}$, and $C_{1212} = C_{44}$. The free energy change corresponding to a thermodynamically reversible elastic deformation of cubic crystals at zero pressure [28] has the form:

$$\begin{aligned}\frac{\Delta F}{V} &= \frac{1}{2}C_{11}\left(\eta_{xx}^2+\eta_{yy}^2+\eta_{zz}^2\right)\\ &+ C_{12}\left(\eta_{xx}\eta_{yy}+\eta_{xx}\eta_{zz}+\eta_{yy}\eta_{zz}\right)\\ &+ 2C_{44}\left(\eta_{xy}^2+\eta_{xz}^2+\eta_{yz}^2\right).\end{aligned} \tag{5}$$

2.1. Equilibrium fluctuation formula (NVT ensemble)

For a central force system, the elastic constants are determined from the analysis of the fluctuations in the positions of the particles in thermodynamic equilibrium using the fluctuation formulas [1,7]:

$$\begin{aligned}C_{\alpha\beta\gamma\tau} &= \frac{1}{V}\left\langle\sum_{i<j}\frac{1}{r^2}\left(\phi''-\frac{\phi'}{r}\right)\Delta x_\alpha^{ij}\Delta x_\beta^{ij}\Delta x_\gamma^{ij}\Delta x_\tau^{ij}\right\rangle\\ &- \frac{1}{VkT}\left\langle\left(\sum_{i<j}\frac{\phi'}{r}\Delta x_\alpha^{ij}\Delta x_\beta^{ij} - \left\langle\sum_{i<j}\frac{\phi'}{r}\Delta x_\alpha^{ij}\Delta x_\beta^{ij}\right\rangle\right)\right.\\ &\times\left.\left(\sum_{i<j}\frac{\phi'}{r}\Delta x_\gamma^{ij}\Delta x_\tau^{ij} - \left\langle\sum_{i<j}\frac{\phi'}{r}\Delta x_\gamma^{ij}\Delta x_\tau^{ij}\right\rangle\right)\right\rangle\\ &+ \frac{NkT}{V}\left(\delta_{\alpha\gamma}\delta_{\beta\tau}+\delta_{\alpha\tau}\delta_{\beta\gamma}\right),\end{aligned} \tag{6}$$

where ϕ is interatomic potential of interaction, the symbol $\langle\cdots\rangle$ designates configurational averages, δ_{ij} is the Kronecker delta, $\Delta x_\alpha^{ij} = x_\alpha(i) - x_\alpha(j)$, and $r = |\Delta x_\alpha^{ij}|^2$. In the case of noncentral interactions, the situation is more complicated and other approaches have to be used, because in general it is impossible to express the elastic energy as a function of the strain tensor [7].

2.2. Strain fluctuation formula (NPT ensemble)

At constant pressure, it is convenient to use the free enthalpy (Gibbs free energy) expansion:

$$\begin{aligned}\frac{\Delta G}{V_p} &= \frac{1}{2}B_{11}\left(\eta_{xx}^2+\eta_{yy}^2+\eta_{zz}^2\right)\\ &+ B_{12}\left(\eta_{xx}\eta_{yy}+\eta_{xx}\eta_{zz}+\eta_{yy}\eta_{zz}\right)\\ &+ 2B_{44}\left(\eta_{xy}^2+\eta_{xz}^2+\eta_{yz}^2\right),\end{aligned} \tag{7}$$

where the volume V_p of the system corresponds to the equilibrium state at p. The elastic constants B_{ij} at pressure p are in the following relation with elastic constants at zero pressure C_{ij}: $B_{11} = C_{11} - p$, $B_{12} = C_{12} + p$, and $B_{44} = C_{44} - p$. In this case, the strain fluctuation formula proposed by Parrinello–Rahman [2] and modified by Ray [4,5] is widely used:

$$B_{\alpha\beta\gamma\tau} = \frac{kT}{V_p}\left[\left\langle\eta_{\alpha\beta}\eta_{\gamma\tau}\right\rangle - \left\langle\eta_{\alpha\beta}\right\rangle\left\langle\eta_{\gamma\tau}\right\rangle\right]^{-1}. \tag{8}$$

Herein the strain tensor is defined as:

$$\eta_{\alpha\beta} = \frac{1}{2}\left(\left\langle\tilde{h}_{\alpha\gamma}\right\rangle^{-1}\tilde{h}_{\gamma\tau}h_{\tau\gamma}\left\langle h_{\gamma\beta}\right\rangle^{-1} - \delta_{\alpha\beta}\right), \tag{9}$$

where h is the matrix that describes the size and shape of the simulation box, matrix $\langle h\rangle$ describes reference box, $\tilde{h}$ is the transpose matrix, and $\left\langle\tilde{h}\right\rangle^{-1}$ is the inverse of the transpose of $\langle h\rangle$. It is convenient to choose the matrices $\langle h\rangle$ and h as symmetric. In this paper a modified version of the Parrinello–Rahman method was used [29,30].

3. Evaluation of the elastic constants using the minimum image method (MIM)

Since the contribution to the elastic constants from long-range interactions cannot be ignored or easily corrected using eqs. analogous to those applicable in the case of the system pressure or energy (2)–(3), a simple extension of the two mentioned above methods is proposed here. It bases on using the minimum image method (MIM) that was previously used for calculations of the energy and pressure in systems with long-range interactions [26,27].

3.1. Minimum image method in the NVT ensemble

The simulations in the canonical ensemble are performed by the standard (Metropolis) Monte Carlo scheme [31]. However the fluctuation formula (6) is applied not only for the particles in the simulation box, but also for their images. The calculations are performed not only for the ith particle with coordinates (x_i, y_i, z_i) but also for its 26 images, so are taken in account the particles with