Monte-Carlo Simulation of a Classical Quadrupole Solid

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The Monte-Carlo method is applied to a sample consisting of 256 linear point-quadrupoles, whose centers are fixed on a face-centered cubic lattice with the usual boundary conditions; the quadrupole interaction is characterized by an energy $\Gamma = \frac{6}{25} \frac{\theta^2}{R_0^5}$. The electrostatic energy is evaluated by means of Ewald-Kornfeld's method. Results are given for energy, specific heat and order parameters and compared with previous papers on the subject. A first-order phase transition is found at $T = (11 \pm 1)\,\Gamma/k_\mathrm{B}$.

I. Introduction

Electrostatic quadrupole interactions are commonly believed to play an important role in various solid systems. They are, at least partly, responsible for transition from hindered to free rotation in N_2 and CO (where the effect of dipole interactions is negligibly small)[1]; dipole and quadrupole interactions govern a similar behaviour in HCl, HBr and HI[1]. Moreover, there is some reason to believe that electrostatic quadrupole interactions play an important role in the upper phase transitions of alkali cyanides NaCN, KCN, RbCN[2]; finally, they are thought to be important among the cerium ions in $\mathrm{Ce(C_2H_5SO_4)_3 \cdot 9\,H_2O}$[3].

In real solids other effects, such as phonon interactions[4], anisotropy of repulsive and dispersive forces[5, 6] and structural changes[6] modify the behaviour due to quadrupolar forces. (In this paper the word quadrupole means linear point-quadrupole.)

A simplified approach to the problem consists of studying a pure quadrupole system, in which the quadrupole centers are fixed in a fcc lattice; the fcc lattice has been chosen because it is the lattice of the molecular centers of mass in some of the above mentioned systems, e. g. low-temperature phases of N_2 and CO.

Reich and Etters[7, 8] have applied a quantum-mechanical treatment to such a system (in the case of N_2); Mandell[9] has applied the classical treatment by means of Monte-Carlo simulation of a sample consisting of 32 particles fixed on a fcc lattice, and considering nearest-neighbour interactions only. The object of the present paper is the Monte-Carlo simulation of a classical, pure-quadrupolar system, whose quadrupolar centers are fixed on a fcc lattice. The calculations were performed on a sample consisting of 256 or 108 particles, in order to obtain some information on the sample size effect; moreover we decided to account for long-range interactions also, which implied the use of Ewald-Kornfeld's algorithm[10, 11], in order to achieve a faster convergence in the evaluation of the electrostatic energy.

Temperatures and energies were expressed in the same units as in Mandell's paper, in order to obtain a straightforward comparison. Let Γ be defined by

$$\Gamma = \frac{6}{25} \frac{\theta^2}{R_0^5} \tag{1}$$

where θ is the quadrupole moment and R_0 is the nearest-neighbour distance; temperatures are given in units Γ/k_B and energies in units $\Gamma \cdot \mathrm{particle}^{-1}$, unless otherwise specified.

II. Formulae of the Ewald-Kornfeld Method[10, 11]

Let us consider a quadrupole with moment θ_1, situated at a point A of space; let its orientation be defined by the unit vector $\boldsymbol{t}_1$. The electrostatic potential it generates in a point P of space is given by

$$V(P) = \frac{\theta_1}{2} (\boldsymbol{t}_1 \cdot \nabla_\mathrm{P})^2 \left(\frac{1}{r}\right); \quad r = |\boldsymbol{r}_\mathrm{P} - \boldsymbol{r}_\mathrm{A}|. \tag{2}$$

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Let us consider a quadrupole $(\boldsymbol{\theta}_2, \boldsymbol{t}_2)$ at a point P in a potential field V; its potential electrostatic energy is

$$U = \frac{\theta_2}{2} (\boldsymbol{t}_2 \cdot \nabla_{\mathrm{P}})^2 (V) . \tag{3}$$

From Eqs. (2) and (3) it follows that the mutual electrostatic energy of two quadrupoles is

$$U_{12} = \frac{\theta_1 \theta_2}{4} (\boldsymbol{t}_2 \cdot \nabla_2)^2 (\boldsymbol{t}_1 \cdot \nabla_1)^2 \left[\frac{1}{r}\right]; \ \boldsymbol{r} = \boldsymbol{r}_2 - \boldsymbol{r}_1 \quad r = |\boldsymbol{r}| . \tag{4}$$

If we define the operator

$$B[f(\zeta)] = \frac{1}{\zeta} \frac{\mathrm{d}f(\zeta)}{\mathrm{d}\zeta} , \text{ for any function } f \tag{5}$$

then Eq. (4) becomes

$$\begin{aligned} U_{12} = \frac{\theta_1 \theta_2}{4} \Big\{ & [1 + 2(\boldsymbol{t}_1 \cdot \boldsymbol{t}_2)^2] B^2 \left(\frac{1}{r}\right) \\ & + [(\boldsymbol{t}_1 \cdot \boldsymbol{r})^2 + (\boldsymbol{t}_2 \cdot \boldsymbol{r})^2 + 4(\boldsymbol{t}_1 \cdot \boldsymbol{r})(\boldsymbol{t}_2 \cdot \boldsymbol{r})(\boldsymbol{t}_1 \cdot \boldsymbol{t}_2)] B^3 \left(\frac{1}{r}\right) \\ & + (\boldsymbol{t}_1 \cdot \boldsymbol{r})^2 (\boldsymbol{t}_2 \cdot \boldsymbol{r})^2 B^4 \left(\frac{1}{r}\right) \Big\} . \end{aligned} \tag{6}$$

Let us now consider a lattice consisting of quadrupoles, all with the same moment θ; let its elementary cell be cubic and contain N quadrupoles, with dimensionless coordinates $\boldsymbol{r}_i = (x_i, y_i, z_i \,|\, 0 \leqq x_i, y_i, z_i \leqq 1)$, and let $\boldsymbol{t}_i$ be the unit vectors defining their orientations; finally, let a be the cell edge length. Note that these hypotheses on the elementary cell are not essential, but they imply a certain simplification of formulae.

In order to evaluate the electrostatic energy of the cell, one could use Eq. (6) in connection with a pair summation:

$$U = \tfrac{1}{2} \sum_{i=1}^{N} \sum_{j}{}' U_{ij} \tag{7}$$

where $\sum_j{}'$ extends all over the lattice and, of course, $i \neq j$. If one does so, the $\sum_j{}'$ turns out to be slowly convergent; a faster convergence can be achieved by means of the Ewald-Kornfeld method which, roughly speaking, consists of using Eq. (4), in which $1/r$ is substituted by its expression according to Ewald's method.

Thus in Ewald-Kornfeld's method the electrostatic energy of the cell is given by

$$U = \frac{\theta^2}{a^5} (U_1 + U_2 + U_3) , \tag{8}$$

$$U_1 = \tfrac{1}{2} \sum_{\boldsymbol{n}}{}' A(\boldsymbol{n}) [C^2(\boldsymbol{n}) + S^2(\boldsymbol{n})] , \tag{9 a}$$

$$A(\boldsymbol{n}) = \frac{4\pi^3}{\boldsymbol{n} \cdot \boldsymbol{n}} \exp\left(-\frac{\pi^2}{\varepsilon^2} \boldsymbol{n} \cdot \boldsymbol{n}\right), \tag{9 b}$$

$$\begin{aligned} C(\boldsymbol{n}) &= \sum_{i=1}^{N} (\boldsymbol{n} \cdot \boldsymbol{t}_i)^2 \cos(2\pi \boldsymbol{n} \cdot \boldsymbol{r}_i), \\ S(\boldsymbol{n}) &= \sum_{i=1}^{N} (\boldsymbol{n} \cdot \boldsymbol{t}_i)^2 \sin(2\pi \boldsymbol{n} \cdot \boldsymbol{r}_i) , \end{aligned} \tag{9 c}$$

$$\begin{aligned} U_2 = \tfrac{1}{4} \sum_{i=1}^{N} \sum_{i=1}^{N}{}' \sum_{\boldsymbol{n}}{}' \{ & [1 + 2(\boldsymbol{t}_i \cdot \boldsymbol{t}_j)^2] B^2(H) \\ & + [\boldsymbol{t}_i \cdot \boldsymbol{\lambda})^2 + (\boldsymbol{t}_j \cdot \boldsymbol{\lambda})^2 \\ & + 4(\boldsymbol{t}_i \cdot \boldsymbol{\lambda})(\boldsymbol{t}_j \cdot \boldsymbol{\lambda})(\boldsymbol{t}_i \cdot \boldsymbol{t}_j)] B^3(H) \\ & + (\boldsymbol{t}_i \cdot \boldsymbol{\lambda})^2 (\boldsymbol{t}_j \cdot \boldsymbol{\lambda})^2 B^4(H) \} , \end{aligned} \tag{10 a}$$

$$\boldsymbol{\lambda} = \boldsymbol{\lambda}(i, j, \boldsymbol{n}) = \boldsymbol{r}_i - \boldsymbol{r}_j + \boldsymbol{n} , \quad \lambda = |\boldsymbol{\lambda}| , \tag{10 b}$$

$$\begin{aligned} H &= H(\lambda) = \frac{1 - \operatorname{erf}(\varepsilon \lambda)}{\lambda} , \\ \operatorname{erf}(u) &= \frac{2}{\sqrt{\pi}} \int_0^u \exp(-\zeta^2) \, \mathrm{d}\zeta , \end{aligned} \tag{10 c}$$

$$U_3 = -\frac{3}{5} \frac{N}{\sqrt{\pi}} \varepsilon^5 . \tag{11}$$

Where $\boldsymbol{n}$ is a dimensionless vector with integer components, and ε is a dimensionless constant whose value effects (in opposite ways) the rates of convergence of the two series, but not the numerical value of U. In U_1 the case $\boldsymbol{n} = (0, 0, 0)$ is excluded, whereas in U_2 the case $j = i$ and $\boldsymbol{n} = (0, 0, 0)$ is excluded. By choosing a suitable value for ε, the series in U_1 can be truncated by the condition $\boldsymbol{n} \cdot \boldsymbol{n} \leqq 16$, and the series in U_2 at $\boldsymbol{n} = (0, 0, 0)$, and the resulting relative error ranges between 10^{-4} and $5 \cdot 10^{-3}$.

By comparing Eqs. (6) and (7) with Eqs. (8) and following, it is easy to recognize that, from the computational point of view, the fundamental difference is given by the term U_1. In the case of Monte-Carlo calculations particles are displaced one at a time so that – provide that the series in U_1 can be truncated soon enough – the use of the Ewald-Kornfeld method implies a tolerable lengthening of the computations, (a typical figure is around 25%). This is balanced by a higher accuracy in the evaluation of the energy.

III. Computational Details

The examined sample is a cube containing $4\,m^3$ ($m = 3$ or 4) particles, whose centers are fixed on a fcc lattice, surrounded by a periodic replica of itself. The computations were started at $T = 2$, with a sample where quadrupoles were arranged in a perfect Pa3 lattice (see Table I). The configuration equilibrated at $T = 2$ was used to start both the production run at $T = 2$ and the equilibration run at $T = 4$, and so on.

Table I. The elementary cell in a Pa3 lattice.

Particle	Coordinates	Orientation
1	$(1/2,\ 1/2,\ 0)$	$(1,\ -1,\ -1)$
2	$(1/2,\ 0,\ 1/2)$	$(-1,\ -1,\ 1)$
3	$(0,\ 1/2,\ 1/2)$	$(-1,\ 1,\ -1)$
4	$(0,\ 0,\ 0)$	$(1,\ 1,\ 1)$

Each particle is described by two angular coordinates; particles are chosen one at a time, in cyclical order. A random variation, uniformly distributed between prescribed bounds, is imposed to each angular coordinate of the chosen particle. The maximum angular displacement allowed varies between $\pm 0.06\,\pi$ radians at $T = 2$ and $\pm 0.60\,\pi$ radians at $T = 32$.

A detailed treatment of the Monte-Carlo method is available elsewhere [12]. The computations were executed on the computer CDC 7600 of the University of London.

IV. Results and Discussion

Most runs were carried out with a sample consisting of 256 particles, and a few with 108, in order to test the sample size effect, which turns out to be small but not negligible (see Table II).

Table II. Sample size effect.

T in units Γ/k_B	U in units $\Gamma\cdot$particle^{-1} 108 particles	256 particles
2	-42.06 ± 0.05	-42.139 ± 0.005
4	-39.67 ± 0.07	-39.89 ± 0.04
6	-37.00 ± 0.26	-37.45 ± 0.06
16	-13.65 ± 0.05	-14.0 ± 0.01

Table III. Comparison of calculated energies.

T in units Γ/k_B	U in units $\Gamma\cdot$particle^{-1} This paper	Ref. 9	M 2, Ref. 15
2	-42.139 ± 0.005	-37.72 ± 0.06	-42.67
4	-39.89 ± 0.04	-35.88 ± 0.16	-40.52
6	-37.45 ± 0.06	-33.66 ± 0.13	-38.17
8	-34.4 ± 0.2	-30.69 ± 0.13	-35.47
10	-29.0 ± 0.2	-27.28 ± 0.81	-32.27
11	-24.1 ± 1.2		-30.32
12	-17.12 ± 0.14	-20.28 ± 0.72	-28.36
14	-15.42 ± 0.08		
15		-15.50 ± 0.13	
16	-14.0 ± 0.1		
18		-13.06 ± 0.19	
20	-11.86 ± 0.02		
24	-10.34 ± 0.05	-10.72 ± 0.13	
28	-9.35 ± 0.04		
30		-8.78 ± 0.19	
32	-8.32 ± 0.05		
40		-6.69 ± 0.22	

Table IV. Comparison of calculated specific heats.

T in units Γ/k_B	C_v in units $k_B\cdot$particle^{-1} This paper	Ref. 9
2	1.11 ± 0.03	1.09 ± 0.14
4	1.58 ± 0.29	1.13 ± 0.19
6	1.24 ± 0.29	1.02 ± 0.14
8	1.76 ± 0.23	2.19 ± 0.33
10	2.4 ± 0.70	3.14 ± 0.55
11	10.9 ± 5.1	
12	0.95 ± 0.10	2.04 ± 0.47
14	0.74 ± 0.07	
15		0.80 ± 0.08
16	0.57 ± 0.04	
18		0.55 ± 0.02
20	0.43 ± 0.02	
24	0.286 ± 0.008	0.38 ± 0.03
28	0.245 ± 0.005	
30		0.261 ± 0.013
32	0.19 ± 0.01	
40		0.148 ± 0.008

Table V. Order parameters. At $T \geqq 14$ both Y_1 and Y_2 are smaller than 0.01 in magnitude.

T in units Γ/k_B	Y_1	Y_2
2	0.99110 ± 0.00001	0.97355 ± 0.00003
4	0.9804 ± 0.0003	0.9424 ± 0.0008
6	0.9680 ± 0.0004	0.907 ± 0.001
8	0.950 ± 0.002	0.857 ± 0.004
10	0.80 ± 0.01	0.745 ± 0.006
11	0.197 ± 0.039	0.578 ± 0.057
12	-0.0071 ± 0.0097	-0.025 ± 0.011

The results listed in Tables III, IV and V were obtained with a sample consisting of 256 particles, and are averages on runs consisting of 450 trials per particle. (600 trials per particle were used at temperatures between 10 and 12.) A similar number of trials was used for equilibration; a comparable number of trials was also used in the runs with a sample consisting of 108 particles.

The statistical errors were calculated from subaverages over sequences of 150 trials per particle. The specific heat was calculated as a fluctuation quantity

$$C_v = \frac{k_B}{N} \frac{\langle U^2 \rangle - \langle U \rangle^2}{(k_B T)^2} . \qquad (12)$$

Where U is the energy of the sample and C_v is expressed in units $k_B \cdot \mathrm{particle}^{-1}$.

The order parameters [13] are defined by

$$Y_1 = \frac{1}{N} \left\langle \sum_{i=1}^{N} P_1(\boldsymbol{\tau}_i \cdot \boldsymbol{t}_i) \right\rangle \quad Y_2 = \frac{1}{N} \left\langle \sum_{i=1}^{N} P_2(\boldsymbol{\tau}_i \cdot \boldsymbol{t}_i) \right\rangle . \qquad (13)$$

Where $\boldsymbol{\tau}_i$ is the unit vector defining the orientation of the i-th particle in a Pa3 lattice, and P are Legendre polynomials.

The following conclusions can be drawn from the listed results:

a) At $T \leqq 8$ our results for the energy are smaller than Mandell's by about 12%; the agreement between the two sets of data improves at $T \geqq 12$, where our values are greater. The agreement between the two sets of values for the C_v appears to be better at $T \leqq 8$ than at $T \geqq 12$, where the statistics has somewhat improved.

b) The values of C_v suggest that the system behaves in an essentially harmonic way at $T \leqq 6$, and anharmonicity sets in rapidly above this temperature.

c) The system exhibits a phase transition, from hindered to free rotation, at $T = 11 \pm 1$: the transition appears to be first order, with a ΔU of $(7 \pm 1)\ \Gamma \cdot \mathrm{particle}^{-1}$. Mandell [9] finds a phase transition at the same temperature and a ΔU of $(3 \pm 1)\ \Gamma \cdot \mathrm{particle}^{-1}$.

In the case of solid α-N_2 we have $R_0 = 3.994$ Å and $\Theta = 1.52 \cdot 10^{-26}$ e.s.u., thus $\Gamma / k_B = 3.95$ K [5, 8] and the transition temperature turns out to be 43 ± 4 K; our value for the ΔU is (230 ± 33) $\mathrm{J \cdot mole^{-1}}$ and Mandell's value is $(99 \pm 33)\ \mathrm{J \cdot mole^{-1}}$. In the case of solid α-N_2, Raich and Etters [8] find a phase transition at $T = 13.77$, i. e. 54.4 K.

The experimental values are $T = 35.6$ K and $\Delta H = 229\ \mathrm{J \cdot mole^{-1}}$ [8, 14]; the agreement between our value of ΔU and the experimental one could be fortuitous.

d) The present results suggest that, at least for an ordered phase, a nearest-neighbour potential is a rather poor approximation.

e) Another paper on this subject has been published recently by Mandell [15]. The Monte-Carlo method is applied there to samples consisting of 108 particles on a fcc lattice and 96 particles on a hcp lattice, moreover first- and second-neighbour interactions are considered; results for the cubic phase are reported there at $T \leqq 13$, and will be referred to as M2.

M2 results for the C_v appear to be affected by rather large statistical errors and to agree with ours at $T \leqq 10$. Smooth curves were fitted by a least square procedure to both energy and specific heat in M2, and the following equations are given in that paper

$$C_v = 1 + \sum_{m=1}^{3} a_m T^m , \qquad (14\,\mathrm{a})$$

$$a_1 = 1.25 \cdot 10^{-2} , \ a_2 = 2.61 \cdot 10^{-3} , \ a_3 = 3.73 \cdot 10^{-4} , \qquad (14\,\mathrm{b})$$

$$U = -44.7 + \int_0^T C_v(T')\, \mathrm{d}T' \qquad (14\,\mathrm{c})$$

where C_v is expressed in units $k_B \cdot \mathrm{particle}^{-1}$. Values of the energy evaluated from Eqs. (14) are reported in Table III; the agreement with our results has remarkably improved.

A first-order phase transition is found in M2 at $T = 12.7 \pm 0.3$, with $\Delta U = 9.1 \pm 1.0$. Long-range interactions, and perhaps sample size effects, appear to be responsible for the difference between the transition temperatures.

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