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Mean-field theory of elastic dipoles on a face-centered-cubic lattice

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Elastic dipole moments, originally devised to describe the interactions between defects in a continuous medium, can also describe the interaction of nonpolar, nonspherical molecules in pure solids at low temperatures. The lowest-energy orientation state of elastic dipoles on an fcc lattice corresponds to the experimentally determined crystal structure of CO_2 and N_2. Mean-field theory predicts a first-order transition from an asymmetric ground state to a random-orientation excited state. We also examine the possibility of a second-order transition involving symmetry breaking in tetrahedral molecules.

INTRODUCTION

Elastic dipoles were originally introduced as a model for the interaction of two or more defects or impurities in a bulk solid.[1,2] It is, however, also possible to extend this model to the interaction between individual molecules in a solid.

The elastic dipole moment Q is a measure of the extent to which an object embedded in an elastic medium disturbs the medium by deviating from sphericity towards being a prolate (positive Q) or an oblate (negative Q) spheroid. Unlike an electric dipole, the elastic dipole and its field are symmetric about the plane perpendicular to the generating object's symmetry axis. The elastic dipole's symmetry properties therefore resemble those of an electric quadrupole rather than an electric dipole. The term *dipole* is used because a pair of symmetrically placed point particles, considered to have both moved out from the origin, generate the elastic dipole field, as well as higher moments. There is nothing corresponding to a negative point charge in elastic multipole theory.

The actual form of the field is as follows. An elastic dipole aligned with the z axis produces a displacement field $\mathbf{u}=Q(2z\hat{\mathbf{z}}-x\hat{\mathbf{x}}-y\hat{\mathbf{y}})/r^3$, where Q is the elastic dipole moment. The field, for positive Q, points away from the source everywhere on the z axis, and towards the source everywhere in the xy plane. There is no difference between the $+z$ and $-z$ orientations of the source, which is taken to have the symmetry properties of a spheroid. Similarly, and of more relevance to the ground state of an array of elastic dipoles in a fcc lattice, as discussed in the next section, there would be no difference between, for example, the (1,1,1) and $(-1,-1,-1)$ orientations for spheroids or for N_2 or CO_2 molecules.

The displacement field $\mathbf{u}$ produces a strain field ε, which, in turn, in the simplest approximation, generates a stress field $\sigma=K\varepsilon$, where K is the bulk modulus of the solid. The strain and displacement can then be combined to give an interaction energy between two elastic dipoles. For example, the energy of interaction between a pair of dipoles oriented in the (1,1,1) and $(1,-1,-1)$ directions with a relative displacement of $R=(X,Y,Z)$ is

$$U=4\pi KQ^2[2YZ-8/3(2X^2-Y^2-Z^2)]/R^5\ ,$$

the interaction between a pair in the (1,1,1) and $(-1,1,-1)$ directions is

$$U=4\pi KQ^2[2XZ-8/3(2Y^2-X^2-Z^2)]R^5\ ,$$

while other combinations of cubic body diagonal orientations give similar functional forms of the interaction energy U.

THE GROUND STATE

A face-centered-cubic lattice with lattice constant a consists of four simple-cubic sublattices with the same lattice constant. We designate the four sublattices as follows: sublattice A centered at (0,0,0), sublattice B centered at $(0,a/2,a/2)$, sublattice C centered at $(a/2,0,a/2)$, and sublattice D centered at $(a/2,a/2,0)$. There are also four possible orientations, each along a cubic body axis. They are designated as orientation a in the $(+1,+1,+1)$ direction, orientation b in the $(+1,-1,-1)$ direction, orientation c in the $(-1,+1,$

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$-1)$ direction, and orientation d in the $(-1,-1,+1)$ direction.

In all that follows, all the molecules of a sublattice will be assumed to be in the same orientation. This will allow us to define system states by assigning one of the four orientations to each of the four sublattices. For example, the system state *aaaa* has all the molecules in all four sublattices in orientation a; while the system state *abcd* has all the molecules on the A sublattice in the a orientation, all the molecules on the B sublattice in the b orientation, all the molecules on the C sublattice in the c orientation, and all the molecules on the D sublattice in the d orientation; and the *acdb* system state has all the molecules on the A sublattice in the a orientation, all the molecules on the B sublattice in the c orientation, all the molecules on the C sublattice in the d orientation, and all the molecules on the D sublattice in the b orientation.

Of the 256 possible system states, there are 8 which share the lowest energy. The 8 states subdivide into two families of 4, with states within a family obtainable from each other by simple translation from one sublattice to another. Each family therefore corresponds to one crystal structure, with the separate states defined around different origins. A change from one of the states within a family to another which did not involve a translation would require changing the orientation of all four sublattices and should be highly unlikely at low temperatures. It is therefore appropriate to treat the states within one family as distinct, even though they all represent the same crystal structure.

The lowest-energy states are as follows, with members of the same family enclosed in square brackets

$$[acdb, bdca, cadb, dbac]; [adbc, bcad, cbda, dacb] .$$

Each family represents a crystal structure with some rotational symmetry, but no reflective symmetry whatever. Reflection about a plane for a state in one family generates a state in the other family. The ground-state crystal structures are therefore a pair of enantiomers. Figure 1 gives a view of the elastic dipole at the origin at its 12 nearest neighbors from a direction slightly above (closer to the z axis) the (1,1,1) direction.

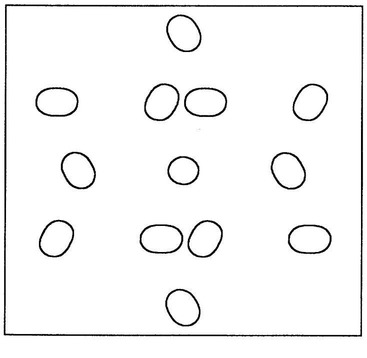

FIG. 1. View of the elastic dipole at the origin and the 12 nearest neighbors from the $(1,1,\sqrt{2})$ direction for the *acdb* (ground) state.

The energy per molecule of these states is

$$-32\pi\sqrt{2}KqQ^2/a^3 ,$$

where $q = 0.54$ is a correction factor due to the inclusion of non-nearest neighbors.

The crystal structure of CO_2 (Ref. 3) and N_2 (Ref. 4) at very low temperatures has been found experimentally to be face-centered cubic with the molecules oriented along cubic body diagonals with the same distribution of orientations among sublattices as in the family containing the *acdb* system state. In addition, with the B, C, and D sublattices in the c, d, and b orientations, the potential at the origin for this model is

$$(-32\pi\sqrt{2}KqQ^2/a^3)(p_{1x}p_{1y} + p_{1y}p_{1z} + p_{1z}p_{1x}) ,$$

for which the a orientation $(p_{1x} = p_{1y} = p_{1z} = +1/\sqrt{3})$ has the overall minimum energy. We therefore take *acdb* as the reference ground state for the mean-field theory.

MEAN-FIELD THEORY

We define a promotion parameter s to describe the behavior at finite temperatures of a system which is in the *acdb* state at zero temperature. s is the relative probability that molecules of one sublattice be in a different orientation from the ground state. System states will have relative probabilities of occupation relative to the ground state of s^n, where n is the number of sublattices which have molecules in orientations different from the ground state. The parameter s ranges from 0, in which case only the ground state is occupied, to 1, which gives all system states an equal probability of being occupied.

A molecule at the origin in the a orientation has an energy of

$$E = (E_0/W)[-q + (-5q + \tfrac{1}{8})s + (-3q + \tfrac{11}{18})s^2 + (9q + \tfrac{17}{24})s^3] ,$$

while a molecule at the origin in one of the other orientations has an energy of

$$E = (E_0/W)[(q/3 + \tfrac{1}{72}) + (5q/3 + \tfrac{11}{54})s + (q + \tfrac{17}{24})s^2 + (-3q + \tfrac{14}{27})s^3] ,$$

where $E_0 = 64\pi\sqrt{2}KQ^2/a^3$, $W = 1 + 9s + 27s^2 + 27s^3$, and the q-independent terms in the energies are from surface terms that arise if two or more sublattices are in the same orientation.

This gives an energy gap of

$$\Delta = (E_0/W)[(4q/3 + \tfrac{1}{72}) + (20q/3 + \tfrac{17}{216})s + (4q + \tfrac{7}{72})s^2 - (12q + \tfrac{41}{216})s^3] ,$$

which yields the self-consistent equation for the promotion parameter

$$s = e^{-\Delta/kT} .$$

s is single valued when $kT < 0.185E_0$, triple valued when $0.185E_0 < kT < 0.228E_0$, and equal to 1 when $kT > 0.228E_0$. A domain simulation gives a first-order

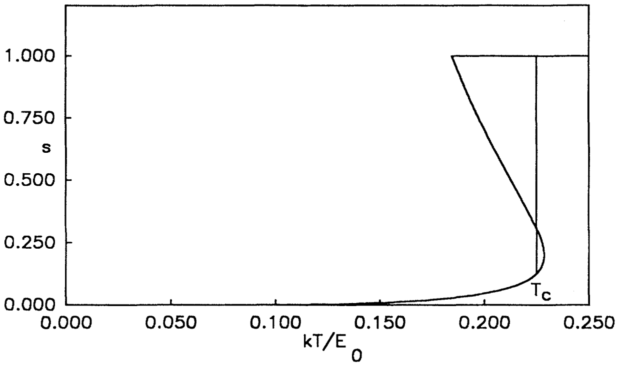

FIG. 2. The promotion parameter s as a function of temperature, including the location of the first-order transition.

transition at $kT=0.2247E_0$. s rises from 0 to 0.124 before the transition, and has a value of 1 everywhere above the transition. The dependence of s on kT/E_0, as well as the location of the transition, is indicated in Fig. 2.

For both CO_2 and N_2, the elastic dipole moment Q has the value $Q=r^3/2$, where r is the distance from the center of the molecule to an end. The crystal structures of the two solids,[3,4] together with the bulk modulus of ice at 50 K,[5] $K=1.128\times10^{10}$ N/m^2, give $Q=0.115$ Å^3, $E_0=1.530$ meV, and $T_c=0.2247E_0/k=4.0$ K for CO_2; and $Q=0.0734$ Å^3, $E_0=0.596$ meV, and $T_c=1.56$ K for N_2.

SECOND-ORDER TRANSITIONS

Of the common tetrahedral molecules, none of the carbon tetrahalides have face-centered cubic structure,[6–8] while methane does.[9,10] The orientation of the methane molecules is undetermined.[9,10] A deformation in the threefold degenerate bending mode produces an elastic dipole moment of

$$Q=\frac{M+4m}{\sqrt{M^2+8Mm+24m^2}}r^2\eta \;,$$

where r is the distance from the central atom to one of the peripheral atoms, M is the mass of the central atom, m is the mass of a peripheral atom, and η is the normal coordinate. Methane yields a value of $E=-qE_0=-0.038$ eV/Å$^2\eta^2$ for the elastic dipole energy per molecule, which compares with the vibrational energy of

$$E=\frac{(3M+4m)(M+4m)}{M^2+8Mm+24m^2}\frac{1}{2}m\omega^2\eta^2=7.723 \text{ eV/Å}^2\eta^2$$

(Ref. 11). The elastic dipole in this case is clearly too weak to produce symmetry breaking.

CONCLUSIONS

Direct application of the simplest version of the elastic dipole model to pure solids, in which individual molecules are treated as spheroids immersed in an isotropic elastic medium, with all the molecules on a sublattice possessing the same one of four allowed orientations, correctly predicts the ground-state orientation of nonpolar, nonspherical molecular solids with a face-entered-cubic lattice. It predicts first-order transitions at temperatures roughly an order of magnitude smaller than those of the actual first-order transitions for the substances examined. Comparison of the elastic dipole and the vibrational energies for methane suggests that a symmetry-breaking second-order transition due to the elastic dipole interaction almost certainly does not take place. This would still be the case even if the elastic constant K were increased to produce correct temperatures for the first-order transitions, or intermediate states and the zero-point energy were included in the calculations, which would have the effect of lowering the first-order transition temperature for a given value of K.

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