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A "Gel" Model for Coal[1]

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Coal is a sedimentary, organic "rock" which is almost never in a state of thermal equilibrium. Because of its importance, the thermal properties of this ill-characterized substance are of great interest. Recent work has shown that coal has many of the characteristics of a gel-type structure. We have made this observation the basis for a model study of the thermal properties of a gel system, using the equation-of-motion method to determine the density of states for the system and, thereby, its heat capacity. This model has one of the essential features of a model of coal, namely, a porous structure. With a hexagonal close-packed lattice as the basis for our gel, we have calculated the frequency spectrum for several particle densities. The disorder in the system has a marked effect on the frequency spectrum, shifting a larger number of modes from high to low frequencies. Also, for a gel with 3% vacancies, and in-plane, out-of-plane bond strengths at the ratio 2: 1, there is a further shift to lower frequencies and the two-peaked spectrum expected for such an anisotropic structure develops. The heat capacity is affected only at low temperatures. We conclude that the gel model provides a satisfactory basis for development as a model of coal.

KEY WORDS: aggregate structure; coal; equation-of-motion method; density dependence; frequency spectrum; "gel" model; harmonic nearest-neighbor forces; heat capacity; hexagonal structure; porous structure.

1. INTRODUCTION

The thermal properties of coal are of considerable current interest as the efficient use of alternative fuel feedstocks becomes a matter of some importance. The structure of coal is poorly defined but recent work has shown that many characteristics of coal are consistent with a gel-type structure

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[1]. This observation has led us to set up such a structure as the framework for a model to study the thermal properties of coal. This model, which is described in Section 2.1, has one of the essential features of coal, namely, a porous structure.

In our present studies, we have two objectives in mind: (i) to develop a versatile, microscopic model to represent coal and (ii) to test the equation-of-motion method as a means of calculating the frequency spectrum of the model system.

In this paper, we present the preliminary results we have obtained. These pertain to three different densities (defined by the number of vacancies in the system, volume V) and, in the lowest-density case, to different interplanar bond strengths. We have calculated the frequency spectrum, energy density, and specific heat in each case.

2. THEORY

2.1. Model

The foundation of our model is a planar triangular array of points. A network of bonds is imposed on this array by a "gelation" procedure [2], thus forming an aggregate structure characterized by the number of bonds inserted and the number of atoms missing. We have constructed a hexagonal close-packed structure by repeating this x–y plane in the z direction. This procedure has the advantage of ensuring the existence of pathways through the system, a feature that is likely to occur in materials such as coal. To increase further the flexibility of the model, we have assigned variable bond strengths to various local configurations of atoms according to the number of bonds filled at any point. We hope, in this way, to mimic the variety of molecular environments in coal. The size of the system currently under investigation is $10 \times 20 \times 6$, permitting a maximum of 1200 atoms. Periodic boundary conditions are imposed on this system to minimize the size effects of a finite system.

2.2. Equation-of-Motion Method

The equation-of-motion method has proved to be a useful way of obtaining the density of states for disordered solids such as amorphous silicon and similar elemental semiconductors [3]. This method utilizes the fact that, for forces of limited range, most elements of the dynamical matrix are zero, and therefore one can solve the equations of motion without recourse to direct numerical diagonalization of the $(3N \times 3N)$ matrix of an N-particle system. The method has been described in detail by von

Heimendahl [4] and co-workers and by Beeman and Alben [3]. Here, we give a brief outline of the method, with details appropriate for our model.

We assume that the atoms interact with nearest-neighbor harmonic forces and express the potential energy of the system as

$$V=\frac{1}{2}\sum_{i=1}^{N}\sum_{j=1}^{12} k_{ij}[(u_i-u_j)\cdot\hat{r}_{ij}]^2 \tag{1}$$

where the summations are over all atoms i in the system and over the 12 nearest neighbors j of each atom in the hcp structure. k_{ij} is the force constant for the bond i–j, u_i is the displacement of atom i from equilibrium, and $\hat{r}_{ij}$ is the unit vector along bond i–j. The equation of motion for the α displacement of atom i, $u_{i\alpha}$, is then given by

$$m_i\frac{d^2u_{i\alpha}}{dt^2}=F_{i\alpha}=-\sum_{j=0}^{12}\sum_{\beta=1}^{3} V_{i\alpha,j\beta}u_{j\beta} \tag{2}$$

where m_i is the mass of atom i and $V_{i\alpha,j\beta}$ is the second derivative of the potential with respect to the displacements $u_{i\alpha}$, $u_{j\beta}$, i.e.,

$$\begin{aligned} V_{i\alpha,j\beta}&=k_{ij}r_{j\alpha}r_{j\beta}, \qquad i\neq j\\ V_{i\alpha,i\beta}&=-\sum_{j=1}^{12} k_{ij}r_{j\alpha}r_{j\beta}\end{aligned} \tag{3}$$

Note that the $V_{i\alpha,j\beta}$ are time independent, therefore they need be calculated only at the outset. From Eqs. (1) and (2), we obtain the components of the force on atom i,

$$F_{ix}=\sum_{j=1}^{12} k_{ij}[(u_{jx}-u_{ix})r_{jx}^2+(u_{jy}-u_{iy})r_{jx}r_{jy}+(u_{jz}-u_{iz})\,r_{jx}r_{jz}] \tag{4}$$

and similarly for the y and z components.

The equations of motion are integrated according to the following scheme, which utilizes the predictor equation of Beeman [5].

(i) The forces are calculated from Eq. (4); and

(ii) at time t, the displacements $u_i(t)$, the velocities $v_i(t)$, and the accelerations $a_i(t)$ are given by

$$\begin{aligned} u_{i\alpha}(t)&=u_{i\alpha}(t-\delta t)+v_{i\alpha}(t-\delta t)\;\delta t+\frac{\delta t^2}{6}\,[4F_{i\alpha}(t-\delta t)-a_{i\alpha}(t-\delta t)]\\ v_{i\alpha}(t)&=v_{i\alpha}(t-\delta t)+\frac{\delta t}{6}\,[5F_{i\alpha}(t-\delta t)-a_{i\alpha}(t-\delta t)]\\ a_{i\alpha}(t)&=F_{i\alpha}(t-\delta t)\end{aligned} \tag{5}$$

With these new displacements, the forces are calculated from Eq. (4) and new velocities are calculated according to the relation

$$v_{i\alpha}(t+\delta t)=v_{i\alpha}(t)+\frac{1}{3}F_{i\alpha}(t)\,\delta t \tag{6}$$

This procedure is repeated to the desired time limit $\mathbb{T}$. The time correlation function,

$$G(t)=\sum_{i=1}^{N}\sum_{\alpha=1}^{3}u_{i\alpha}(0)\,u_{i\alpha}(t) \tag{7}$$

is calculated at each step. We also monitor the kinetic energy,

$$E_{\mathrm{k}}(t)=\frac{1}{2}\sum_{i=1}^{N}\sum_{\alpha=1}^{3}v_{i\alpha}(t)^2 \tag{8}$$

and the potential energy [Eq. (1)].

The initial conditions for this scheme are as follows:

$$\begin{aligned} v_{i\alpha}(0)&=0\\ a_{i\alpha}(0)&=0\\ u_{i\alpha}(0)&=2\cos\varphi_{i\alpha} \end{aligned} \tag{9}$$

where the $\varphi_{i\alpha}$ are random angles uniformly distributed over one cycle. With this prescription [3], the frequency distribution $f(\omega)$ is given by

$$f(\omega)=\frac{2}{\pi}\int_0^{\mathbb{T}}G(t)\cos(\omega t)\exp(-\lambda^2 t)\,dt \tag{10}$$

where λ is a spreading factor. Using the suggestions of Beeman and Alben as a guide, we have taken the time step δt to be 1/20 of τ, the shortest period in the system, and we have set $\lambda=9/\mathbb{T}^2$. Satisfactory statistics were obtained with the following values:

$$\delta t=0.04,\qquad \frac{k}{m}=10,\qquad \text{and}\quad \mathbb{T}=600\,\delta t \tag{11}$$

The units of δt and k/m are such that the maximum frequency of the hcp lattice is given by

$$\omega_{\mathrm{L}}=\frac{2\pi}{\tau}=\frac{\pi}{10\delta t}=\sqrt{\frac{6k}{m}} \tag{12}$$

For statistical purposes, the correlation function $G(t)$ in Eq. (10) must be averaged over a number of different initial configurations. We found that 50 configurations were sufficient to give stable results.

2.3. Specific Heat

Once we have the frequency distribution for the system, we can calculate the internal energy and the specific heat from the well-known relations [6]

$$E = \frac{3N}{F}\int_0^{\omega_L} \frac{h\omega f(\omega)\, d\omega}{(e^{\beta}-1)} \tag{13}$$

$$C_V = \frac{3Nk_B}{F}\int_0^{\omega_L} \frac{\beta^2 e^{-\beta} f(\omega)\, d\omega}{(e^{\beta}-1)^2} \tag{14}$$

where

$$F = \int_0^{\omega_L} f(\omega)\, d\omega \tag{15}$$

We use the notation, $\beta = (h\omega/k_B T)$, where k_B is the Boltzmann constant and T is the temperature in kelvin. The frequency scale is set by Eq. (12) and the relation

$$\omega_L = 250\,\delta\omega \tag{16}$$

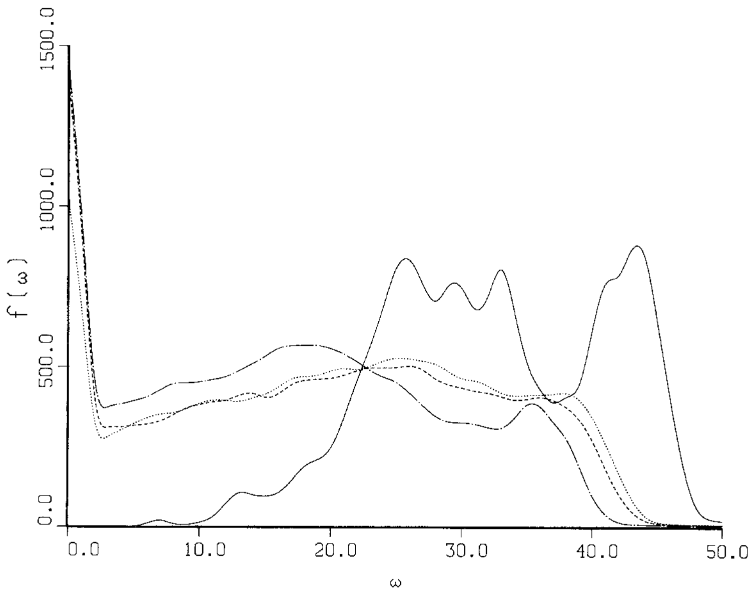

Fig. 1. Frequency spectrum for aggregates of different density. hcp lattice (1200 particles), ——; 1188 particles, ····; 1164 particles, – – –; 1164 particles with half-strength bonds in the z direction, –·–.

3. RESULTS

First, we calculated the frequency distribution, the internal energy, and the heat capacity of the perfect hcp lattice, i.e., $c/a = 1.63$, all 1200 atoms were present, and all bonds were of equal strength. The results provide a reference for the subsequent calculations and a check on our procedures. The results for $f(\omega)$ and $C(T)$ are shown in Figs. 1 and 2 and are typical of a monatomic lattice. Next, we selected an aggregate with 1164 atoms present (3 % vacancies) and repeated the calculation. As can be seen from Fig. 1, the frequency distribution is drastically altered by the disorder in the system, but since the change is most pronounced at very low frequencies, the qualitative behavior of the specific heat is unaltered. Since this system has a rather large concentration of vacancies, we repeated the calculation for another aggregate having 1 % vacancies (1188 atoms), with similar results. Finally, to reflect better the type of bonding that is thought to be present in coal, we have also considered the case where the bonds in the z direction are weaker than those in the x–y plane. A two-peaked structure is apparent in the frequency spectrum, as we would expect in such an anisotropic situation, the low-frequency peak being associated with vibrations in the z direction.

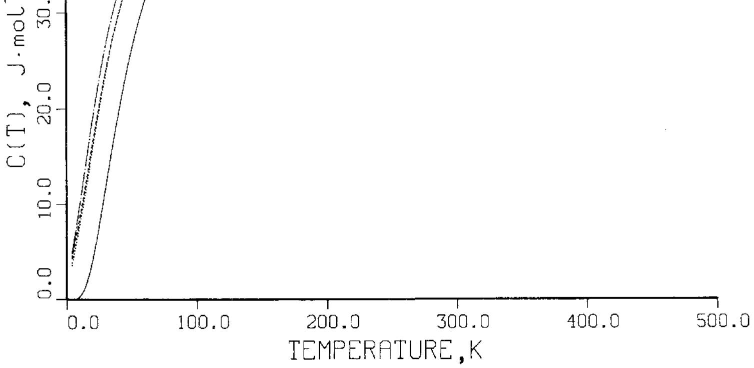

Fig. 2. Variation of heat capacity, $C(T)$, with density of aggregate. hcp lattice (1200 particles), ——; 1188 particles, ····; 1164 particles, ----; 1164 particles with half-strength bonds in the z direction, –·–.

4. DISCUSSION

We have tested the equation-of-motion method and find that it is a satisfactory way to determine the frequency spectrum of a disordered solid. The low-frequency peak that occurs in the frequency spectrum of the disordered lattices may be evidence of relaxation in the aggregate structure [7]. We do not claim that the results presented here, for what is still a comparatively simple and well-ordered structure, are representative of coal, however, they do provide a basis upon which to build a more realistic theory. As it stands, the model has the capability for considerable variation in the structural units that comprise the system via the variable bond strengths. It also provides a framework for the study of diffusion in porous media, through the pathways that exist in the structure. Both of these features must be incorporated into any description of coal. Further elaboration of the model might include foreign atoms trapped at sites with unfilled bonds or molecules at each site instead of neutral atoms, to name just two of the developments that we envisage. To be fruitful, development of the model must be guided by a close collaboration with experimental investigations of coal structure. We look forward to tackling some of these problems in the future.

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