Vibrational Anomalies Are Not Generally Due to Fractal Geometry: Comments on Proteins

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Deviations in a d-dimensional Euclidean connected lattice of the spectral number (cumulative) of vibrational states from the frequently generalized formula $N(\omega) \propto \omega^d$, i.e., density $\rho(\omega) \propto \omega^{d-1}$, are common at very low frequency in many materials (e.g., crystalline), and are not related to disorder or fractal connectivity. These anomalies have been shown to be due to strong anisotropy, or to noncentral molecular-type forces, or both. The apparent spectral densities seen in globular and sheet proteins are compatible with conventional theoretical models dominated by molecular bond-bending or torsional forces.

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Recently there has been much discussion of the *dynamics* of polymers, biological molecules, glasses, and other nontraditional materials. Simultaneously, new insights, particularly the concept of fractals,[1] have developed to describe the *structure* of various disordered network materials. Orbach[2] and others have developed theories of vibrational spectra on fractals, proposing that anomalous vibrational-state densities occur in frequency regimes determined by the fractal structure. While we do not question that possibility, it is the purpose of this Letter to show that the inverse conclusion—anomalous vibrational spectra imply fractal structure—cannot generally be drawn on either experimental or theoretical grounds. We also call attention to the fact that the unqualified assertion that the cumulative vibrational-state density $N(\omega) \propto \omega^d$ in a Euclidean connected structure, and conclusions derived therefrom, are generally irrelevant except in a world of cubic, square, or linear lattices, with central forces and at *very* low frequency. Deviations from this unjustifiably generalized *Ansatz* are widely found in crystalline materials, as a result of anisotropy and important noncentral forces, and are familiar in chemistry and materials science.

Of particular recent interest are the experimental and theoretical studies by Stapleton[3] and co-workers on the vibrational spectra in proteins. Fractons (i.e., fractal phonons) have been proposed as the source of "anomalies" in the temperature dependence of the (Raman) two-phonon electron-spin relaxation rate of low-spin ferric-ion-containing proteins. Since these observations are potentially of considerable biological importance, it is important to explore all possible alternative explanations; it is our view that there is no compelling need to invoke fractal concepts to explain the *dynamics.*

Before proceeding to a discussion of the underlying physical and theoretical basis for the assertions above, we call attention to the history of experimental studies of the heat capacity in a number of "anomalous" materials. Figure 1 shows data for a variety of materials, *all good 3D crystalline samples.* Gallium and graphite[4] show accurately a T^2 dependence of C_v from 10 to 40 K; crystalline selenium[5] yields $C_v = k_s T^n$ with $n = 1.38$, $T = 25$ K; $n = 1.71$, $T = 20$ K; $n = 2.56$, $T = 15$ K; i.e., not really a power law! Not shown are diamond,[6] quartz,[7] cristobalite, and vitreous silica[8]; all show excess density of states ($T/\theta \sim 0.05$) which cannot be deduced from elastic-constant data. Nor can these be assigned specifically to an amorphous structure; indeed Bilir and Phillips[8] show that crystalline cristobalite and vitreous silica have essentially the same heat capacity, and their neutron spectra[9] are not significantly different. In fact, it is likely that the principal anomalies are quite adequately explained as due to rocking motions of SiO_4 tetrahedra[10,11] superim-

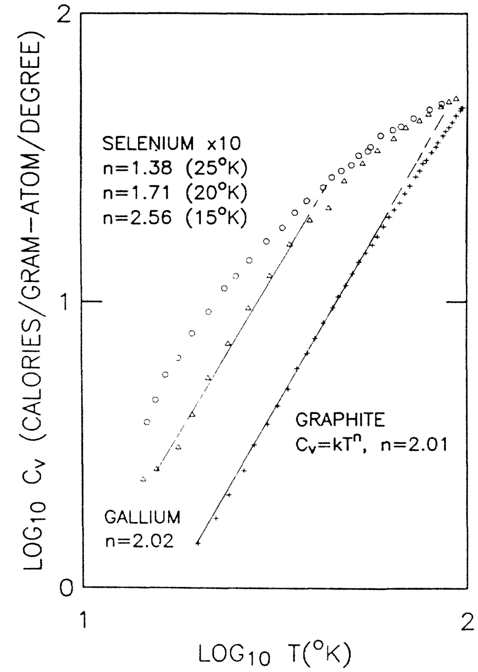

FIG. 1. Anamolous heat capacity of *crystalline* gallium, graphite, and selenium. [After DeSorba (Refs. 4 and 5).]

posed on the normal T^3 term. Moreover, the anomalous heat capacity of crystalline germanium has been clearly traced to noncentral forces.[12]

We proceed next to discuss in physical terms why (A) strong anisotropy and (B) noncentral forces vitiate the generality of the "ω^d principle." While the discussion here is qualitative, the application to graphite was studied both experimentally[13] and theoretically[14] to high precision in the period 1950–1965 for highly perfect crystalline (3D) graphite where $N(\omega)=\omega^{d-1}$ over several decades except below 2 K; it serves as a teaching example. We also note in passing that considerations similar to those reviewed here have been appearing in studies of the elasticity of percolating networks.[15] Central forces yield different scaling relations from bond-bending forces, and crossover effects occur. Unfortunately, two-center force models, which cannot simulate angular or torsional forces, and are not invariant under rigid rotation, are frequently used uncritically in computer simulations.

Consider (A) first, the consequence of strong anisotropy in the atomic interactions. A widely used phenomenological theory for discussing the heat capacity of such systems was put forth and applied to a variety of substances by Tarasov[16-18] and has been used widely in discussing polymers and anisotropic materials. For example, for a crystal composed of interacting chains,

$$C_{1(3)}=3R\left(\frac{T}{\theta_1}\right)\int_{\theta_3/T}^{\theta_1/T}\frac{x^2e^x}{(e^x-1)^2}dx+\frac{9RT^3}{\theta_1\theta_3}\int_0^{\theta_3/T}\frac{x^4e^x}{(e^x-1)^2}dx. \tag{1}$$

This expression exhibits a crossover from T^3 behavior below $T\simeq\theta_3$ to a linear heat capactiy at higher temperature. In crystalline polymers[17] and other chainlike lattices[18] θ_3 may range from a few degrees to tens of degrees Kelvin.

An analogous expression applies to layered materials. For the case of graphite Tarasov's phenomenological method was placed on a quantitative footing by Krumhansl and Brooks.[14] In brief, their derivation was as follows: (i) For a highly anisotropic crystal with widely spaced layers, an appropriate dispersion relationship for phonons has the form

$$\omega^2=c_\parallel^2(k_x^2+k_y^2)+2(c_\perp^2/\tau_\perp^2)(1-\cos k_\perp\tau_\perp). \tag{2}$$

Here $\tau_\perp$ is the spacing between layers, $c_\parallel$ and $c_\perp$ are the in-plane and perpendicular sound speeds, respectively, and the long-wave approximation has been assumed for the fast propagation along layers. (ii) To calculate the total number of states having frequency up to ω one needs to know the volume enclosed in k space by the surface $\omega=\text{const}$. (iii) The maximum frequency for purely perpendicular propagation is ω_3 $(c_\perp/\tau_\perp)$, and this is the crossover frequency below which $N(\omega)\propto\omega^3$, but above which the Brillouin zone is truncated and $N(\omega)\propto\omega^2$. The resulting formula closely resembles Tarasov's but provides additional interpolation terms, demonstrating one possible source of deviations from $N(\omega)\propto\omega^d$ without recourse to anomalous connectivity. Generally, except for the crossover region $\omega\simeq\omega_3$, where the constant-frequency ellipse just touches the Brillouin zone,

$$\begin{aligned}&N(\omega)\propto\omega^3, && \omega<\omega_3,\\ &N(\omega)\propto\omega, && \omega>\omega_3, \quad \text{chains},\\ &N(\omega)\propto\omega^2, && \omega>\omega_3, \quad \text{layers}.\end{aligned} \tag{3}$$

In essence, in highly anisotropic materials there are various "Debye" temperatures, some very low indeed, which give rise to anomalous state density and specific heat.

However, as time went on, deviations from Tarasov's formula were frequently found, and further measurements on graphite gave contradictory values of elastic constants, between heat-capacity and elastic measurements.[19,20] It then became apparent more or less simultaneously to a number of investigators,[20] that when one addressed loosely packed chains or layers the central forces (which are pairwise) might be less important than "bond bending" and "dihedral twist" molecular forces (three and four center, respectively). As it turned out, the introduction of these resolved the contradiction in graphite to a highly quantitative degree, but the physical concepts are applicable generally and present a fundamentally different source of deviation from the canonical density-of-states formula, case (B).

Molecular valence-bond forces were modeled[21] by potential functions more recently familiar in liquid-crystal theory. Thus, for pure bending motion and transverse displacements $u(x,t)$, $\rho u=\sigma_\parallel^4(\partial^4/\partial x^4)u$, whence $\omega^2=\sigma_\parallel^4k_\parallel^4$. In addition, for chains interacting weakly, interchain terms lead to a dispersion relation (for long waves)

$$\omega^2=c_\perp^2(k_x^2+k_y^2)+c_\parallel^2k_z^2+\sigma_\parallel^4k_z^4. \tag{4}$$

There is now a new "nongeometric" crossover frequency ω_x determined by $c_\parallel^2=\sigma_\parallel^4k_z^2$, $k_x=0=k_y$. Calculating the appropriate volume of k space of various systems, one finds

$$\begin{aligned}&N(\omega)\propto\omega^3, && \text{always}, \quad \omega<\omega_x,\\ &N(\omega)\propto\omega^{5/2}, && \text{bendable interacting chains}, \quad \omega>\omega_x,\\ &N(\omega)\propto\omega^2, && \text{bendable interacting layers}, \quad \omega>\omega_x,\\ &N(\omega)\propto\omega^{3/2}, && \text{bendable blob}, \quad \omega>\omega_x.\end{aligned}$$

Note the amusing fact that this source of spectral anomaly leads in the case of layers to the same dependence, $N(\omega) \propto \omega^2$, as the anistropy anomaly. This alternative was first noted by Komatsu[20] for graphite, and subsequently confirmed quantitatively by the author and others.[19,22] The $\omega^{5/2}$ dependence for chain crystals also appeared in a specific model for a polymer crystal proposed by Stockmayer and Hecht.[23]

While the above is qualitatively correct for simple linear molecules the actual situation for real molecules is clearly more complicated. It appears[24] that there is a choice between either of two representational bases: (a) Use Cartesian coordinates for each atom, in which case the mass matrix is diagonal but the potential matrix must include many-center interactions explicitly to properly represent bending and torsional forces; or (b) use natural variables such as bond angles or torsional (dihedral) angles, in which case the mass matrix is not diagonal. Mean-field models generally do not take these factors into account, yet those are just the ingredients which can produce low-frequency variations from the simple Debye rule.

It is now interesting to note the consequences of regarding a globular protein as a bendable blob. What is envisaged is that the low-frequency modes of globular stuctures are primarily isotropic, shear in nature, and resisted by bending forces in the polypeptide chain. At the very, very lowest frequencies $N(\omega) \propto \omega^3$; but above the crossover frequency, $N(\omega) \propto \omega^{3/2}$ and $\rho(\omega) \propto \omega^{1/2}$. The observations by Stapleton and coworkers[3] on a number of globular proteins yield various exponents close to this, and the low-frequency density of states computed by Go, Noguti, and Nishikawa[25] for the protein bovine pancreatic trypsin inhibitor (BPTI) can be fitted well with an exponent of 0.5. On the other hand, Daurel, Delhaes, and Dupart[26] measured the heat capacity of β-sheet poly (L-valine) protein and found that the data could be fitted nicely by a 2D Tarasov model between 2 and 300 K, with $\theta_3 \sim 25$ K and $\theta_2 \sim 130$ K; however, as noted above, in "2D" structures either the bond-bending or Tarasov models lead to the same temperature dependence. The concepts above can be extended further in many directions. For example, in some models of purely torsional forces one can find the dispersion $\omega^2 \propto \kappa^6$. In combination with other interactions, it is quite possible to reproduce state densities $\rho(\omega)$ with exponents $\frac{1}{3}$, $\frac{2}{3}$, and other; the ways in which this can be done need not be unique. Further detailed study is called for.

In summary, the main purpose of this communication is to recall and emphasize that anisotropy and molecular bending forces in themselves are sufficient to explain a wide variety of observed deviations from the $N(\omega) \propto \omega^d$ rule, which is not universal in any practical sense. Qualitatively, protein *dynamics* seem to be in accord with state densities expected of bond-bending and twisting models. This is not surprising since the main degrees of freedom are of this type. A more quantitative application of these methods to recent experiments will be presented elsewhere.

We close with a general comment on the dynamics of fractals. There is no doubt that globular materials exist with mass fractal dimension D such that the mass $M(r) = Br^D$ and $D < 3$. However, there certainly are cases where this dimension is irrelevant to the molecular dynamics. Specifically, consider a loosely (fractally coiled) chain composed of monomer units interacting strongly with their immediate neighbors only. The spatial irregularity has nothing to do with the structure of the dynamical matrix describing the harmonic motion, as long as the sequence of monomer variables can be ordered one to one on the diagonal with only nearby off-diagonal elements. If the units are nearly identical, there is effectively translational symmetry for mathematical purposes. The loss of density periodicity in laboratory space is more or less irrelevant to the eigenvalue problem. In fact, there is an extensive chemical literature on *n*-alkanes, paraffins, polyethylene, etc., where vibrational spectra are computed as "ω vs phase," not "ω vs k".[27]

I am indebted to Harvey Stapleton for stimulating my interests in these issues in biopolymers, to Robert Pohl and Bernhard Wunderlich for sharing with me their encyclopedic knowledge of phonons in crystalline materials and polymers, respectively, and to Chris Henley for comments. We hope that we have not followed the advice of an old German theorist to one of his younger collegues: "Warum einfach machen wenn es kompliziert sein kann es ist so schön?" Partial support for this work was received from the U.S. Naval Air Systems Command.

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