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The relation of the Grüneisen parameter to the fractal dimension

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Abstract

Based on both the definition and experimental data, we propose that the inverse of the Grüneisen parameter γ is directly related to the fractal dimension. Scaling behavior of vibrational frequency versus volume extends over large distances via constructing the relation of the Grüneisen parameter to the interatomic force constant for some alkali halides with an NaCl structure. In particular, these alkali halides should possess a universal class with $\gamma = 1.245$. © 2001 Elsevier Science B.V. All rights reserved.

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Derivations and applications of Grüneisen parameter rest heavily on the fundamentals of statistical, quantum and solid-state physical theory. The necessary simplicity of the real atomic systems for which the theory applies and the incredible complexity of its highly theoretical basis have severely limited this parameter's practicality for most substances [1]. However, as it appears in many valuable equations of state for materials at high temperatures and pressures and as its range of numerical values is much narrower than all other thermodynamic quantities, Grüneisen parameter persists to be fashionable in the geophysical literatures [2–6].

Although Quareni and Mulargia [4] compiled several formulations of the Grüneisen parameter for the purpose to derive thermodynamic properties of the Earth's interior, we will concentrate the present study on the mode Grüneisen parameter. By differentiating the Helmholtz free energy with respect to the volume V at constant temperature, Grüneisen introduced a dimensionless quantity, the mode Grüneisen parameter $-\left(\partial \ln \omega_i / \partial \ln V\right)$, in an equation of state (EOS) [1]. In the definition ω_i represents the frequency for a given normal mode of vibration in a crystal lattice. Assuming the frequencies of all the vibration modes are the same, Mie-Grüneisen EOS is obtained. Thus, all mode Grüneisen parameters can be replaced with a single value which is often denoted by

$$\gamma = -\frac{\partial \ln \omega}{\partial \ln V}. \quad (1)$$

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It is noted that since the vibrational frequency is inversely proportional to the wavelength λ when the wave velocity is constant, γ could be rewritten in the following form:

$$V = A\lambda^{1/\gamma}, \quad (2)$$

where A is a constant of proportionality. Eq. (2) shows a power-law distribution of crystal vibrations. Mandelbrot [7] extended the general rule $measure(length) \sim (length)^D$ from conventional Euclidean dimension, for which the exponent D is strictly an integer (e.g. the volume is a cubic measure and proportional to the cube of length), to the fractal dimension, for which D is not necessary an integer. There has developed a growing interest in the fractal properties of natural objects in the last two decades. Many objects in nature have a self-similar fractal spatial structure implying that systems are correlated over large distances. Eq. (2) obviously suggests that the scaling exponent $1/\gamma$ behaves like a fractal dimension.

The log–log plot of $\omega(V)$ versus V usually displays a linear relationship between $\log \omega$ and $\log V$ [6], thus showing power-law scaling. The slope of a best-fitting line to the data points is the Grüneisen parameter, which might have a relation with the fractal dimension. There exists many experimental data [6,8–10], revealing the validity of scaling behavior in lattice vibrations during compression for most materials. However, only a small percentage of volume, in general, can be compacted in the high-pressure experiments. The scale invariance of fractal properties usually extends over several orders of magnitude in length. On the other hand, the fact that γ remains a constant over large amounts of compression seems unclear. This is a plausible reason for the fact that so far γ has never been considered as the fractal dimension in any literature. In the following, based on the treatment of Born and Huang [1], we relate available values of γ to the interatomic force constants [11] for the alkali halides of NaCl structure. So we may extend the effect of the change in volume upon the vibrating frequency to test the validity of scaling behavior in lattice vibrations over large length scales.

A typical approach to study the lattice vibrations is the application of a linear harmonic chain of oscillators with nearest-neighboring interactions

[1]. The vibration of atoms in the chain is governed by the equation of motion

$$m_j \frac{d^2 u_j}{dt^2} = k_{j,j+1} u_{j+1} + k_{j,j-1} u_{j-1} - (k_{j,j+1} + k_{j,j-1}) u_j, \quad (3)$$

where u_j is the displacement of the j th atom with mass m_j from its equilibrium position; and $k_{j,j+1}$ and $k_{j,j-1}$ are the strengths of the couplings between two neighboring atoms, in other words, the interatomic force constants. In the case of NaCl-type structure, we replace m_j by m for the cation and M for the anion, and because of the symmetry it is reasonable to assume all the strengths of the couplings between neighboring atoms have the same value, that is $k_{j,j+1} = k_{j,j-1} = C$. Provided that the time dependence in Eq. (3) behaves like $u_j \propto \exp(-i\omega t)$, the stationary equation of motion is obtained. Upon diagonalization [1], one may calculate the eigenfrequencies ω of the normal mode

$$\omega^2 = C \left(\frac{m+M}{mM} \right) \left[1 \pm \sqrt{1 - \frac{4mM}{(m+M)^2} \sin^2(aq)} \right], \quad (4)$$

where a and q represent the spacing of two nearest atoms in equilibrium state and the wavelength of lattice vibrations, respectively. Putting the periodic boundary condition in the linear chain [1], only the interatomic force constant C in Eq. (4) depends on the volume/length of the chain, and consequently Grüneisen parameter is

$$\gamma = - \frac{\partial \ln \omega}{\partial \ln a} = - \frac{\partial \ln C^{1/2}}{\partial \ln a} = - \frac{1}{2} \frac{\partial \ln C}{\partial \ln a}. \quad (5)$$

It is remarkable that Eq. (5) reveals the mechanical meaning of Grüneisen parameter, and Eq. (2) shows its geometric meaning. This implies that a geometric parameter can reflect mechanical behavior.

Grimvall and Guillermet [11] reported a relationship between the interatomic force constant C and the volume V for some alkali halides (Fig. 1). The dashed line shown in Fig. 1, with a slope of -0.83 , gives a crude description of C versus V for some alkali halides of NaCl structure. With $V \sim a^3$, the slope of -0.83 in Fig. 1 corresponds to

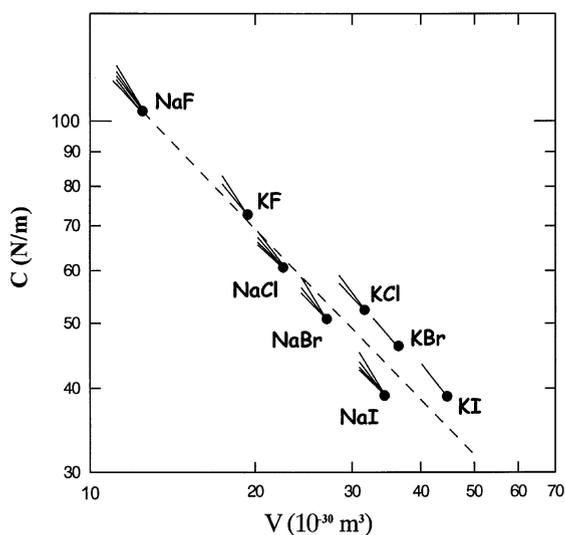


Fig. 1. A logarithmic plot of the average interatomic force constant C versus volume V for some alkali halides with NaCl structure (after Grimvall and Guillermet [11]). The dashed line corresponds to $CV^{0.83} = \text{constant}$. Several short solid lines, corresponding to γ listed in Table 1, represent 10% of compression in volume for these alkali halides.

$\gamma = 1.245$, based on Eq. (5). The short solid lines, corresponding to several given values of γ shown in Table 1, indicate 10% of compression in volume for these alkali halides. As mentioned in many high-pressure studies [6,8–10], constant γ was considered during the small amounts of compression. A remarkable feature in Fig. 1 is that the values of Grüneisen parameter for these alkali halides with NaCl structure are almost around 1.245 over large volume scales. The scaling property for a certain material during volume compression indicates short-range self-similarity, and that for different alkali halides demonstrates long-range self-similarity.

Up to the present, we have realized that according to both the definition and experimental results, the inverse of the Grüneisen parameter behaves like the fractal dimension in crystals. Such a fractal dimension describes the scaling of lattice thermal vibrations and this standpoint provides another important content of Grüneisen parameter. A fractal energy spectrum in quasiperiodic structures recently raised a great number of theoretical and

Table 1

Grüneisen parameters γ (upper subcells) and slopes (lower sub-cells) of interatomic force constant C versus volume V for some alkali halides with NaCl structure. γ was transferred to the slope of $\log C$ versus $\log V$ via $\gamma = -\frac{3}{2} \partial \ln C / \partial \ln V$. The standard deviations in parentheses are expressed in units of the last digit

	Ref. [1]	Ref. [12]	Ref. [13]	Ref. [14]	Ref. [15]
NaF	1.57	2.02	1.62 (60)	1.77	1.37
	−1.05	−1.35	−1.08	−1.18	−0.91
NaCl	1.43	1.12	1.17 (195)	1.62	
	−0.95	−0.75	−0.78	−1.08	
NaBr	1.55		2.07 (55)	1.27	
	−1.03		−1.38	−0.85	
NaI	1.59	1.22	2.02 (25)	1.27	
	−1.06	−0.81	−1.35	−0.85	
KF	1.48				1.87
	−0.99				−1.25
KCl	1.34	1.67			
	−0.89	−1.11			
KBr	1.43				
	−0.95				
KI	1.58				
	−1.05				

experimental works [16–19]. Like this study, these works remarkably show intrinsic fractal properties of crystals.

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