

THE ELASTIC CONSTANTS OF THE DISORDERED PHASE OF SF₆: A COMPUTER SIMULATION CALCULATION

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The elastic constants of SF₆ in the orientationally disordered phase have been calculated by molecular dynamics computer simulations, and the results compared with experimental measurements. Although the calculated elastic constants are consistently lower than the experimental values, suggesting that the model intermolecular potential is too soft, the overall trends observed in the experiments are reproduced well. This allows us to use the results of other simulation calculations to interpret the effect of bilinear rotation-translation coupling on the elastic constants. One result of this study is to show that no elastic anomaly is associated with the ordering phase transition at 96 K.

1. Introduction

Sulphur hexafluoride (SF₆) has an orientationally disordered (OD) phase that exists between 96 and 223 K. Neutron powder diffraction studies have shown that this phase has a body-centred cubic lattice, with the S-F bonds lying close to the $\langle 001 \rangle$ directions [1]. Computer simulations have shown that the OD arises from a competition between different orientational interactions, giving rise to an orientational frustration that is resolved dynamically [2]. As this effect is particularly dominant in SF₆, and because there is no statistical component to the disorder (in the traditional sense), SF₆ has become a model system for study.

Recent interest has focused on the behaviour of the acoustic modes in this system. A preliminary inelastic neutron scattering investigation of the acoustic modes in SF₆ showed that at most wavevectors they are overdamped [3]. This observation was confirmed by computer simulation calculations [3], which, however, predicted the existence of a crossover in behaviour from oscillation-propagating collective acoustic excitations at small wavevectors to damped motions at larger wavevectors. This crossover has recently been confirmed by inelastic neutron scattering [4]. In addition, the existence of well-defined acoustic modes at small wavevectors has been

observed in Brillouin scattering measurements [5]. It was suggested that the origin of this crossover is due to the existence of a strong coupling between the acoustic modes and the rotational modes [3], the so-called "rotation-translation" coupling [6]. The crossover occurs when the acoustic phonon frequencies become comparable to the relaxation frequencies of the rotational motions. This picture has been confirmed by our recent neutron scattering measurements [4] together with further simulation calculations [7]^{#1}.

The purpose of this Letter is to present some simulation calculations of the elastic constants of SF₆ in the OD phase, following the recent experimental measurement of these quantities [5]. There are two main aims in presenting the comparison of the calculated and measured elastic constants. The first is to provide an assessment of the intermolecular potentials used in our recent set of simulations [2,3,7,8]. The second is to enable us to use the results of our simulations in the interpretation of the experimental results.

^{#1} Preliminary results have been published by Dove and Lynden-Bell [8].

2. Details of calculation

The results have been obtained with the molecular dynamics simulation technique using 4096 rigid molecules in the classical microcanonical ensemble. Many of the details associated with these simulations were presented elsewhere [2]. The intermolecular potential was modelled using a Lennard-Jones atom-atom interaction for F...F contacts,

$$V(r) = -4\epsilon[(\sigma/r)^6 - (\sigma/r)^{12}], \quad (1)$$

where r is an F...F interatomic distance, $\epsilon = 0.586$ kJ mol⁻¹ and $\sigma = 2.70$ Å [9]. This model has been shown to give a good representation of the main characteristics of the real SF₆ system, including details of the ordering phase transitions [2-4,10,11]. It is known, though, that the model potential is slightly softer than the true potential [2,10], but the essential physical properties reproduced by this model are not affected by this deficiency.

The elastic constants were obtained from calculations of the harmonic fluctuations of the acoustic normal mode coordinates $Q(\mathbf{k})$, which are given as the spatial Fourier transforms of the molecular displacements parallel (longitudinal acoustic) or perpendicular (transverse acoustic) to the wavevector \mathbf{k} [7,8]. Although the phonon modes are overdamped for all larger values of \mathbf{k} , it is possible to define an effective quasi-harmonic frequency

$$\omega^2(\mathbf{k}) = k_B T / \langle Q(\mathbf{k}) Q(-\mathbf{k}) \rangle, \quad (2)$$

where T is the temperature, and the brackets $\langle \rangle$ denote an average over time. At small wavevectors the frequencies of the propagating acoustic modes are consistent with this definition. The fluctuation amplitudes were calculated for \mathbf{k} along the [001], [101] and [111] directions, and were used to obtain sets of dispersion curves. The elastic constants were obtained by fitting to the gradients of the dispersion curves in the limit $\mathbf{k} \rightarrow 0$. It should be noted that this method was used instead of direct thermodynamic calculations of the elastic properties because the results presented here were obtained as a by-product of a wider study of the collective properties of SF₆ [7] rather than as an end in themselves. Since thermodynamic methods and this method both involve ensemble fluctuations, they are expected to be of similar accuracy.

The calculations were performed at three temperatures over the stability of the OD phase, 115, 150 and 200 K.

3. Results and discussion

The calculated elastic constants are in table 1. To allow comparison with experimental results, the calculated values are also shown in fig. 1 with the measured values [5].

The first point noted from the comparison in fig. 1 is that the simulation consistently underestimates the elastic constants. This indicates that the intermolecular potential is too soft; this conclusion had already been drawn from previous simulation calculations of the disordered phase [2] and static lattice energy calculations of the ordered low-temperature phase [10]. The second point we note from the comparison is that despite this uniform underestimate, the trends observed in the experiments are reproduced in the calculation. In particular, the

Table 1
Calculated values of the elastic constants of SF₆. The units are 10⁹ N m⁻². Standard deviations on the last significant figures are given in parentheses

T (K)	C_{11}	C_{12}	C_{44}
115	4.77(23)	2.00(9)	1.22(6)
150	4.31(37)	2.19(19)	1.27(11)
200	2.73(14)	1.40(7)	1.14(5)

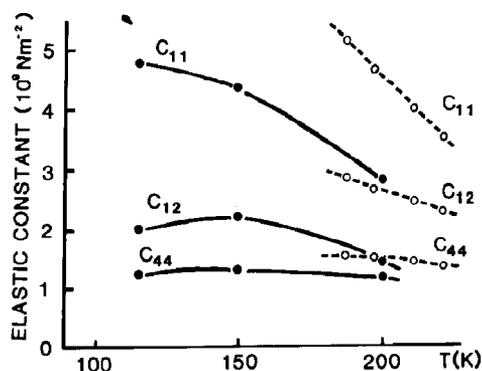


Fig. 1. Calculated (filled circles) and measured (open circles) elastic constants in SF₆. The curves are drawn as guides to the eye.

order of the elastic constants, $C_{11} > C_{12} > C_{44}$, is reproduced, and the ratios of the different elastic constants are similar in the calculations and experiments. Furthermore, the simulations reproduce the temperature dependence of the elastic constants, namely $\partial C_{11}/\partial T > \partial C_{12}/\partial T > \partial C_{44}/\partial T$. Particularly encouraging is the fact that the simulations have accurately reproduced the steep fall of C_{11} with increasing temperature around 200 K. This means that we can reasonably use the simulation to interpret the experimental measurements (see the comments at the end of the first paragraph in section 2). In particular, it has been noted [5] that none of the elastic constants show any anomalous temperature dependence, and neither are the ratios of the elastic constants or sound velocities unusually large. This is different from other orientationally disordered crystals, so does this imply that the rotation-translation coupling interactions [6] are weak in SF_6 ?

Recent simulations [7,8] have shown that the bilinear rotation-translation coupling in SF_6 is reasonably strong in the limit $k \rightarrow 0$ for both the longitudinal and transverse acoustic modes. Therefore all the acoustic modes will be softened as a result of this coupling. However, this coupling in all cases is only weakly temperature dependent, since it is not part of the main driving mechanism of the ordering phase transition; it will not cause any anomalous temperature dependence of the elastic constants. The simulations [7,8] predict that C_{44} is softened by 50% to 30% of its "bare" value (that is the value it would have in the absence of bilinear rotation-translation coupling) over the temperature range 115 to 200 K, respectively. Similarly C_{11} is predicted to soften uniformly by 20% from its bare value over the same temperature range. It has been pointed out [5] that the ratio $(C_{11}/C_{44})^{1/2}$ is not anomalously large in SF_6 , whereas this ratio is often found to be large in OD crystals due to rotation-translation coupling. Using the simulation results quoted above [7,8], we can predict that the rotation-translation coupling will cause the ratio $(C_{11}/C_{44})^{1/2}$ to be increased above its bare value by only 26% to 7% over the temperature range 115 to 200 K. The ratio $(C_{11}/C_{44})^{1/2}$ is therefore expected to increase on cooling, as observed both in the experiments [5] and simulations (present results). We conclude that the experimental results are consistent with the existence of reasona-

bly strong rotation-translation coupling that affects both the longitudinal and transverse modes, and which therefore does not give rise to an anomalous value for the ratio $(C_{11}/C_{44})^{1/2}$. The increase in this ratio on cooling is explained by an increase in the coupling involving the transverse modes. However, it is also clear that the bare elastic constants have significant temperature dependence at high temperatures, which is presumably due to anharmonic effects and associated with the approaching melting point.

Because the rotation-translation coupling is not directly involved in the ordering phase transition in SF_6 (which involves ordering wavevectors for which the rotation-translation coupling vanishes), it does not lead to the striking anomalous behaviour of the elastic constants as seen in KCN for example [6], and is therefore never as strong as that calculated in the isomorphous NaCN [12]. Nevertheless, this coupling in SF_6 still affects both the collective dynamics [4,7,8] and the details of the structural distortions associated with the ordering phase transition [11].

It is worthwhile comparing the simulation calculations with the results of a previous harmonic lattice dynamics calculation [9] for SF_6 in an idealized fully ordered body-centred-cubic structure using the same potential model as in the simulation. The lattice dynamics calculation predicted an imaginary (i.e. unstable) value for C_{44} , which by analogy with standard soft-mode phase transitions would predict that the ordering phase transition would involve a softening of C_{44} . This is not the case; the dynamic disorder which stabilises the cubic structure has completely changed the behaviour so that comparison with a harmonic ordered model is not possible.

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