

## LETTER TO THE EDITOR

# Vibrations and melting of an icosahedral polytope

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**Abstract.** Polytope 120, a perfect icosahedral crystal in non-Euclidean three-dimensional space, models local icosahedral order in metallic glasses. We utilise the symmetries of polytope 120 to determine its vibrational spectrum, Debye–Waller factor and Lindemann's constant. The melting temperature of the icosahedral crystal is twice as large as the melting temperature of an FCC crystal. Enhanced stability against melting arises from the greater stiffness and larger Lindemann's constant of the icosahedral polytope.

Polytope 120 is a close-packed icosahedrally coordinated crystal with 120 atoms embedded in  $\mathbb{S}^3$ , the curved three-dimensional surface of a sphere in four-dimensional space [1]. Several authors use the polytope 120 to model local icosahedral order in metallic glasses. It is believed that metallic glasses, Frank–Kasper crystals and quasi-crystals share the same local icosahedral order as polytope 120 [2–9]. It is energetically favourable for atoms interacting with attractive central forces to form icosahedral clusters, in which 20 tetrahedra with small distortions are packed together around a central point. This idea has been used to explain the large supercooling of undercooled liquids [6]. Icosahedral order cannot be extended throughout  $\mathbb{R}^3$  because of the icosahedron's five-fold symmetry and icosahedral frustration. In Frank–Kasper crystals [7] there are regions of icosahedral order threaded by an ordered array of disclination lines. Metallic glasses may be described as Frank–Kasper phases in which the disclination lines have become entangled [3, 8].

In this Letter we present the result of a calculation of the mean square displacement  $\langle r^2 \rangle$ , where  $r$  is the displacement of an atom vibrating around its equilibrium position in polytope 120. From the value of  $\langle r^2 \rangle$  we determine the Debye–Waller factor which describes the effects of thermal vibrations of atoms on the structure function of the polytope 120. We also estimate Lindemann's constant of the polytope 120, the ratio of the root mean square of  $r$  to the separation of nearest neighbours, by evaluating the mean square displacement at the temperature at which the polytope melts.

We find that  $\langle r^2 \rangle$  varies linearly with temperature in the harmonic approximation, so the Debye–Waller factor decreases exponentially as a function of temperature. At a given temperature the mean square atomic displacement is greater in an FCC crystal than in the polytope. In addition, the Lindemann's constant of the polytope is larger than the corresponding Lindemann's constant of an FCC crystal so at their melting points the vibrational amplitude is greater in the polytope than in an FCC crystal. In other words, the polytope 120 is more stable than an FCC crystal against thermal motions in two

respects: the polytope vibrates less at a given temperature, but can withstand greater amplitude vibrations without melting.

To evaluate the mean square displacement we solve the equations of motion for atoms moving on  $S^3$  interacting through a pair potential. We construct the vibrational eigen-functions explicitly by requiring that they transform under irreducible representations of  $G$ , the symmetry group of the polytope [9]. Then we derive a force operator acting on an atom for an arbitrary potential  $V(r)$  within the harmonic approximation. The vibrational frequencies are readily extracted from the eigenvalues of the force operator.

To classify the vibrational spectrum of the polytope according to irreducible representation of  $G$ , we use techniques from molecular vibration theory. First of all, one finds the total representation  $T$  given by all the vibrational coordinates (basis vectors) together, then decomposes it into irreducible representations of  $G$  (see table 1). The basis vector at position  $\hat{u}$  is defined as [9]

$$\psi_{\alpha\beta}(\hat{u}) = \frac{1}{120(Y')} \sum_{l \in Y'} \chi_{\alpha}^{Y'}(l) \chi_{\beta}^{Y'}(l^{-1}\hat{u}) l \hat{e}_z l^{-1} \hat{u}. \quad (1)$$

**Table 1.** Vibrational eigenvalues  $\lambda_{\alpha\beta}$  and  $\Lambda_{\alpha\beta}$  and degeneracy  $d_{\alpha\beta}$  according to irreducible representation.

| $\alpha\beta$ | $d_{\alpha\beta}$ | $\lambda_{\alpha\beta}$ | $\Lambda_{\alpha\beta}$ |
|---------------|-------------------|-------------------------|-------------------------|
| Longitudinal  |                   |                         |                         |
| $E_1E_1$      | 4                 | 10.61803399             | 1.118033989             |
| $F_1F_1$      | 9                 | 7.472135955             | 0.4270509831            |
| $G_1G_1$      | 16                | 4.045084972             | -0.2725424859           |
| $HH$          | 25                | 1                       | -0.8090169944           |
| $II_1$        | 36                | -2.716579672            | 0.1977591197            |
| $II_2$        | 36                | -1.137522293            | -1.079725131            |
| $G_2G_2$      | 16                | -3.281152949            | -0.3454915028           |
| Transverse    |                   |                         |                         |
| $F_1A$        | 6                 | 9.708203932             | 1.381966011             |
| $G_1E_1$      | 16                | 6.472135955             | 1.118033989             |
| $HF_1$        | 30                | 3                       | 0.8090169944            |
| $IG_1$        | 48                | 0                       | 0.5                     |
| $F_2H$        | 30                | -2                      | 0.3819660113            |
| $G_2H$        | 40                | -2                      | 0.118033989             |
| $G_2F_2$      | 24                | -2                      | -1.118033989            |
| $E_2I$        | 24                | -3                      | -0.4270509831           |

This produces a basis vector of a tangential irreducible representation of  $G$  for all  $\alpha\beta \in T$  except for  $\alpha\beta = II$ , for which it produces a sum of basis vectors of the two occurrences of  $II$  in  $T$ ,

$$\psi_{II}(\hat{u}) = \psi_{II_1}(\hat{u}) + \psi_{II_2}(\hat{u}). \quad (2)$$

Let  $V(r)$  be the interaction between atoms and the equilibrium separation between atoms be  $s = 1$ , so the curvature is  $\kappa = \Omega$ , the Golden Mean. Without loss of generality we may take the atom at the North pole as a particular one and study its response to displacement of nearest neighbours  $V_1$ , because each atom has the same environment.

Displacing each atom of the polytope to another position on  $\mathbb{S}^3$  by a small displacement  $\varepsilon\psi(\hat{u})$ , we find that the total force exerted on the North pole is

$$F_{\text{tot}} = A \sum_{V \in V_1} (1 - V) + A\varepsilon \sum_{V \in V_1} (\psi_{\alpha\beta}(V) - \psi_{\alpha\beta}(\mathbf{1})) \\ + B\varepsilon \sum_{V \in V_1} (V - \mathbf{1})(1 - V) \cdot (\psi_{\alpha\beta}(V) - \psi_{\alpha\beta}(\mathbf{1})) \quad (3)$$

$$= C(1 + \varepsilon\psi_{\alpha\beta}(\mathbf{1})) - [A(\lambda_{\alpha\beta} - \lambda_{F_{1A}}) + B(\Lambda_{\alpha\beta} - \Lambda_{F_{1A}})]\varepsilon\psi_{\alpha\beta}(\mathbf{1}) \quad (4)$$

where  $A, B$  are coefficients related to the form of the interaction  $V(r)$  [10]. The first term in equation (4) above is normal to  $\mathbb{S}^3$  and is discarded since atoms are confined to move in  $\mathbb{S}^3$  only.

Now because the functions  $\psi_{\alpha\beta}$  are eigen-functions of  $F_{\text{tot}}$ , we may write

$$\sum_{V \in V_1} \psi_{\alpha\beta}(V) = \lambda_{\alpha\beta} \psi_{\alpha\beta}(\mathbf{1}) \quad (5)$$

$$\sum_{V \in V_1} (V - \mathbf{1})(V - \mathbf{1}) \cdot \psi_{\alpha\beta}(V) = \Lambda_{\alpha\beta} \psi_{\alpha\beta}(\mathbf{1}) \quad (6)$$

where  $\lambda_{\alpha\beta}$  and  $\Lambda_{\alpha\beta}$  are vibrational eigenvalues. The final form of the force operator acting on an eigen-function is

$$F^t[\psi_{\alpha\beta}(\mathbf{1})] = -[A(\lambda_{\alpha\beta} - \lambda_{F_{1A}}) + B(\Lambda_{\alpha\beta} - \Lambda_{F_{1A}})]\varepsilon\psi_{\alpha\beta}(\mathbf{1}). \quad (7)$$

Values of  $\lambda_{\alpha\beta}$  and  $\Lambda_{\alpha\beta}$  are listed in table 1.

This general force operator is suitable to any kind of pair potential. For the sake of comparison with Monte Carlo simulations, we adopt a purely repulsive inverse 12th potential

$$V(r) = 4/r^{12}. \quad (8)$$

In this case  $A = 48$ ,  $B = -48 \times 14/(2 - \Omega)$ . The vibrational spectrum can be readily obtained through

$$\omega_{\alpha\beta}^2 = A(\lambda_{\alpha\beta} - \lambda_{F_{1A}}) + B(\Lambda_{\alpha\beta} - \Lambda_{F_{1A}}). \quad (9)$$

With the spectrum, we are able to calculate the mean square displacements of atoms from their equilibrium positions in the polytope. The displacement of an atom is due to the superposition of all the normal modes. Thus the mean square displacement is

$$\langle r^2 \rangle_{\text{poly}} = \frac{1}{N} \sum_{\alpha\beta} \langle (r_{\alpha\beta} \psi_{\alpha\beta}(\hat{u}) \cdot \hat{e}_\gamma)^2 \rangle \\ = \frac{1}{N} \sum_{\alpha\beta} \langle (r_{\alpha\beta})^2 \rangle \\ = \frac{1}{N} \sum_{\alpha\beta} \int \pi_{\alpha\beta} \, dr_{\alpha\beta} \exp\left(-\sum_{\alpha\beta} \frac{1}{2} \omega_{\alpha\beta}^2 r_{\alpha\beta}^2 / k_B T\right) r_{\alpha\beta}^2 / Z \\ = \frac{k_B T}{N} \sum_{\alpha\beta} \frac{1}{\omega_{\alpha\beta}^2} \quad (10)$$

where  $N$  is number of atoms which is 120 and  $Z$  is the partition function. Substituting the values of  $\omega_{\alpha\beta}^2$  obtained from (9) into (10), we have

$$\langle r^2 \rangle_{\text{poly}} = 0.0023 k_B T. \quad (11)$$

This is a linear function of temperature  $T$ , but of course it cannot be valid over the whole temperature range. As one increases the temperature the amplitude becomes larger and larger, and eventually a temperature is reached at which the amplitude is so large that the polytope simply melts. One would expect the expression to break down before melting occurs, but as we shall see it is quite good up to the melting point.

It is intriguing to compare (11) with the corresponding quantity for an FCC crystal, which is a close-packed structure in three-dimensional flat space. We can easily generalise (10) to three-dimensional flat space

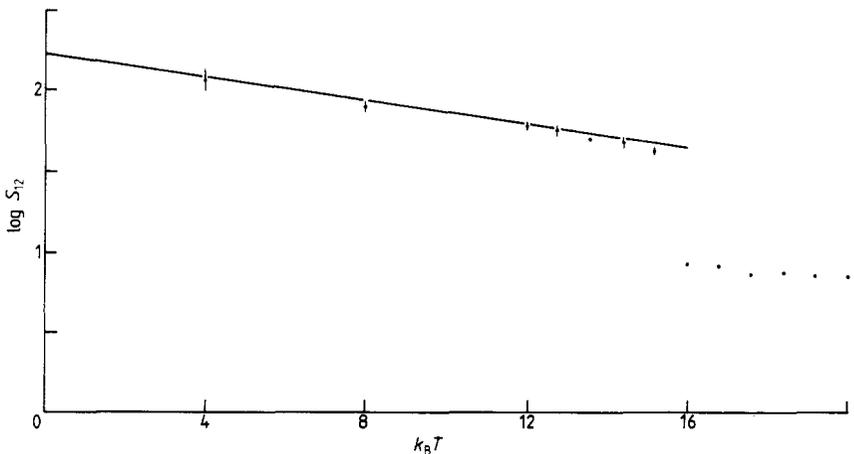
$$\langle r^2 \rangle_{\text{FCC}} = k_B T \int_{B_1} d\mathbf{k} \text{Tr} D^{-1}(\mathbf{k}) / \int_{B_1} d\mathbf{k} \quad (12)$$

where  $D(\mathbf{k})$  is the dynamical matrix of an FCC crystal with an inverse 12th potential and unit neighbouring distance [10] and  $B_1$  is the first Brillouin zone:

$$\langle r^2 \rangle_{\text{FCC}} = 0.0027 k_B T. \quad (13)$$

Thus at a given temperature the thermal vibrational amplitude of the polytope is smaller than the thermal vibrational amplitude of an FCC crystal. The icosahedral crystal is more stiff than the cubic crystal. The difference may be attributed to soft transverse phonon modes in the [110] direction of the cubic crystal.

The Debye–Waller factor describes the effects of thermal vibrations of atoms about their equilibrium positions. It reduces the intensities of Bragg peaks or the values of the structure function of a crystal. Straley has simulated the motions of atoms of the polytope [11]. He calculated the structure function of the polytope as a function of temperature and found a sudden jump at  $T_m$ , which is recognised as the melting temperature,  $k_B T_m = 16$  (see figure 1).



**Figure 1.** Structure function  $S_{12}$  versus temperature. (Note: Some of the error bars are too small to be drawn). The full line is the theoretical prediction (equation (18)).

We derive a formula for the Debye–Waller factor of the polytope, compare it with Straley’s data, and find that the formula is in excellent agreement with Straley’s simulation results all the way up to the melting temperature.

$$\begin{aligned}
 S_n(T) &= \frac{1}{(n+1)^2} \sum_{\hat{R}_1 \hat{R}_2, m_1 m_2} \langle Y_{nm_1 m_2}(\hat{R}_1) Y_{nm_1 m_2}^*(\hat{R}_2) \rangle \\
 &= \frac{1}{(n+1)^2} \sum_{\hat{R}_a \hat{R}_b, m_1 m_2} \langle \exp(-i\kappa L_{0\mu}^{(n)} \cdot \mathbf{r}_a(0)) \exp(+i\kappa L_{0\mu}^{(n)} \cdot \mathbf{r}_b(t)) \rangle \\
 &\quad \times Y_{nm_1 m_2}(\hat{R}_a) Y_{nm_1 m_2}^*(\hat{R}_b)
 \end{aligned} \tag{14}$$

where  $\hat{R}_1, \hat{R}_2$  are the positions of atoms displaced from  $\hat{R}_a, \hat{R}_b$  respectively and  $\mathbf{r}_a(0)$  and  $\mathbf{r}_b(t)$  are the amplitudes of atoms at  $\hat{R}_a$  and  $\hat{R}_b$ .  $L_{0\mu}$  is the curved space analogue of a ‘translation’ in the  $\mu$  direction. If we keep only the zero-phonon contribution, we obtain

$$S_n(T) = \frac{1}{(n+1)^2} \sum_{\hat{R}_1 \hat{R}_2, m_1 m_2} \exp[-\kappa^2 \langle (L_{0\mu}^{(n)} \cdot \mathbf{r})^2 \rangle] Y_{nm_1 m_2}(\hat{R}_a) Y_{nm_1 m_2}^*(\hat{R}_b) \tag{15}$$

$$\begin{aligned}
 &= \frac{1}{(n+1)^2} \exp[-\kappa^2 n(n+2) \langle r^2 \rangle_{\text{poly}}/4] \sum_{\hat{R}_a \hat{R}_b, m_1 m_2} Y_{nm_1 m_2}(\hat{R}_a) \\
 &\quad \times Y_{nm_1 m_2}^*(\hat{R}_b)
 \end{aligned} \tag{16}$$

$$= \frac{120}{n+1} \exp[-\kappa^2 n(n+2) \langle r^2 \rangle_{\text{poly}}/4] \tag{17}$$

$$= \exp[-\kappa^2 n(n+2) \langle r^2 \rangle_{\text{poly}}/4] S_n(T=0). \tag{18}$$

Note the factor of 4 in the exponent which differs from the usual factor of 3 because the polytope is embedded in four-dimensional space. (Note that  $S_n$  vanishes [8] except when  $n = 0, 12, 20, 24 \dots$ )

The agreement suggests that the harmonic approximation works well, and it gives us confidence about our calculations even at the melting temperature. Lindemann’s constant is such a quantity measured at the melting temperature. It is the ratio of the root mean square of  $r$  to the nearest separation between atoms. For the polytope, combining (9) with  $k_B T_m = 16$ , we find that

$$L_{\text{poly}} = 0.19. \tag{19}$$

We also carry out the calculation of this physical quantity using density functional theory with Straley’s data on the structure function of the polytope in its liquid phase. It is interesting to note that the values obtained are in reasonable agreement although there are unresolved problems with density functional theory itself [12].

The corresponding problem has been studied by computer simulation for an FCC crystal with the inverse 12th potential and unit neighbour distance between atoms [13], and Lindemann’s constant was found to be

$$L_{\text{FCC}} = 0.15. \tag{20}$$

$L_{\text{poly}}$  is about 20% larger than  $L_{\text{FCC}}$ , so at the melting temperature the thermal vibrational amplitude of polytope 120 is much greater than the thermal vibrational

amplitude of an FCC crystal. The ratio of the polytope melting temperature to the FCC melting temperature may be calculated from

$$\frac{T_m(\text{poly})}{T_m(\text{FCC})} = \frac{L_{\text{poly}}^2 \langle r^2 \rangle_{\text{FCC}}}{L_{\text{FCC}}^2 \langle r^2 \rangle_{\text{poly}}} = 1.9$$

in agreement with the finding of Straley.

Thus polytope 120 has greater stability against thermal motions than an FCC crystal does. The polytope consists solely of tetrahedral cells, whereas an FCC crystal contains a mixture of tetrahedral and octahedral cells in a ratio 2:1. There are soft modes in certain directions [10] in an FCC crystal because the tetrahedral cells resist distortions more effectively than octahedral cells do. The soft modes, which reduce the crystal's rigidity, are suppressed in the isotropic polytope [9] leading to enhanced thermal stability.

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