



Rigid units revisited

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Like any shopper, thermodynamics loves a bargain: the most active degrees of freedom in a chemical species will always be those that are cheapest to excite. In isolated molecules, the lowest-energy degrees of freedom are translations and rotations. On the other hand, in the simplest crystal structures, such as metals or alkali halides, atomic-scale translation and rotation are no longer possible, and the lowest-energy degrees of freedom become long-wavelength acoustic modes.

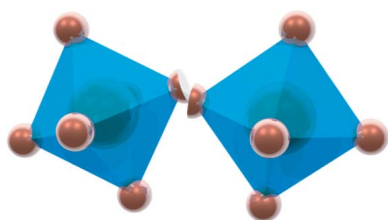
Many more complex solids, however, fall somewhere between the two. Consider, for instance, silicates made up of a network of corner-sharing SiO_4 tetrahedra. It will be energetically expensive to distort individual tetrahedra, but much cheaper to allow the network to flex about the oxygen atoms that connect their corners. Thus the most thermally accessible modes will include those that involve no deformation of the tetrahedral geometry: the so-called *rigid-unit modes*.

Rigid unit mode analysis has been applied not just to the silicates (Hammonds *et al.*, 1996) but to other materials ranging from oxides to cyanides (Goodwin & Keper, 2005) and more complex coordination polymers (Zhou *et al.*, 2008), in both crystalline and amorphous phases. This analysis was central to the first geometric explanations of negative thermal expansion – the property whereby a material contracts, rather than expanding, when heated (Pryde *et al.*, 1996; Dove & Fang, 2016) – and of associated anomalous thermodynamic properties such as pressure-induced softening (Fang & Dove, 2013). One particularly longstanding area of applicability is the distortions of the perovskite structure, which has been an active research field since the well known first observations of soft modes in SrTiO_3 (Shirane & Yamada, 1969) and catalogue of the phases that can arise from such modes ‘freezing in’ (Glazer, 1972).

How can we calculate the rigid-unit modes available to any given structure? A simple and effective answer was given by Giddy and co-workers (Giddy *et al.*, 1993) and implemented in their program *CRUSH* (Hammonds *et al.*, 1994). In this method, each atom joining two rigid units is split in two and joined by a stiff spring of equilibrium length zero. The dynamical equations can then be constructed exactly as for any other potential model. Since real atoms are not divided neatly into halves in this way, most solutions to this model will be meaningless, but those at zero frequency – where the springs are unstretched and each atom remains whole – will correspond exactly to the RUMs.

In this issue, a team led by Campbell proposes an elegant alternative to this approach (Campbell *et al.*, 2018). Representing each rigid-unit rotation as a vector, they linearize the effect of each rotation on each shared atom, effectively considering an infinitesimal rotation. Since adjacent polyhedral units must rotate in such a way that they continue to have any shared atoms in common, the result is a system of linear equations. In the language of crystal structure refinement, one might say that this algebraic approach uses *constraints* to prevent shared atoms from being split, in contrast with the *CRUSH* method that uses *restraints* to the same end (Fig. 1). The team further refine their approach by using group-theory techniques to represent the problem in terms of symmetry-mode amplitudes rather than individual rotations.

The result is an easy and widely applicable methodology to calculate the RUMs associated with any specified set of interconnected rigid units, within the confines of a chosen subgroup. The authors demonstrate their approach on both classic (perovskite, β -quartz) and less well studied (tungsten bronze) systems, revealing in the latter case RUMs that have not previously been reported.



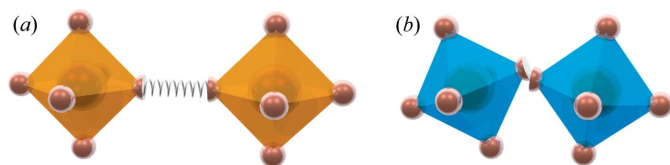


Figure 1

(a) The *CRUSH* approach to identifying rigid-unit modes involves stiff springs joining the two hypothetical halves of an atom. (b) The new approach of Campbell *et al.* instead requires zero mismatch (or sufficiently small mismatch in the case of quasi-RUMs) between the rotating adjacent units in order to avoid the type of splitting illustrated.

Two aspects of the authors' proposed further work are noteworthy. First, they anticipate incorporating their work into the widely used *ISOTROPY* software suite (H. T. Stokes, D. M. Hatch & B. T. Campbell, <http://iso.byu.edu>). The existence of user-friendly web-based tools such as this and the Bilbao Crystallographic Server (Aroyo, Perez-Mato *et al.*, 2006; Aroyo, Kirov *et al.*, 2006) has brought the exceptional power of computer-based symmetry analysis to widespread use among the crystallographic community. Computer analyses have historically provided several corrections to results achieved 'by hand', for instance in the distortion modes of perovskites (Howard & Stokes, 1998), and may yet do so again in this case.

Second, the authors suggest that their method may be extended to the 'quasi-RUMs'. Despite the attractiveness of the model's neat division into RUMs and distortive modes, of course in a real solid there is a continuum between coordination polyhedra remaining rigid and distorting drastically. In fact, modes involving only slight distortions are often equally important to a material's thermodynamic properties, especially when they extend over a larger region of the Brillouin

zone than the RUMs. Application of the new method to such modes would therefore be especially welcome.

Interest in anomalous thermodynamic behaviour, from both scientific and technological viewpoints, shows no signs of abating. Similarly, displacive phase transitions, especially those leading to ferroic phases, continue to be highly relevant. Identifying RUMs and their relatives will thus continue to be an important task, and Campbell *et al.* have contributed a neat and effective tool for this purpose.

References

- Aroyo, M. I., Kirov, A., Capillas, C., Perez-Mato, J. M. & Wondratschek, H. (2006). *Acta Cryst. A* **62**, 115–128.
- Aroyo, M. I., Perez-Mato, J. M., Capillas, C., Kroumova, E., Ivantchev, S., Madariaga, G., Kirov, A. & Wondratschek, H. (2006). *Z. Kristallogr.* **221**, 15–27.
- Campbell, B., Howard, C. J., Averett, T. B., Whittle, T. A., Schmid, S., Machlus, S., Yost, C. & Stokes, H. T. (2018). *Acta Cryst. A* **74**, 408–424.
- Dove, M. T. & Fang, H. (2016). *Rep. Prog. Phys.* **79**, 066503.
- Fang, H. & Dove, M. T. (2013). *Phys. Rev. B*, **87**, 214109.
- Giddy, A. P., Dove, M. T., Pawley, G. S. & Heine, V. (1993). *Acta Cryst. A* **49**, 697–703.
- Glazer, A. M. (1972). *Acta Cryst. B* **28**, 3384–3392.
- Goodwin, A. L. & Kepert, C. J. (2005). *Phys. Rev. B*, **71**, 140301.
- Hammonds, K. D., Dove, M. T., Giddy, A. P. & Heine, V. (1994). *Am. Mineral.* **79**, 1207–1209.
- Hammonds, K. D., Dove, M. T., Giddy, A. P., Heine, V. & Winkler, B. (1996). *Am. Mineral.* **81**, 1057–1079.
- Howard, C. J. & Stokes, H. T. (1998). *Acta Cryst. B* **54**, 782–789.
- Pryde, A. K. A., Hammonds, K. D., Dove, M. T., Heine, V., Gale, J. D. & Warren, M. C. (1996). *J. Phys. Condens. Matter*, **8**, 10973–10982.
- Shirane, G. & Yamada, Y. (1969). *Phys. Rev.* **177**, 858–863.
- Zhou, W., Wu, H., Yildirim, T., Simpson, J. R. & Walker, A. R. H. (2008). *Phys. Rev. B*, **78**, 054114.