Madelung Energy and Bragg Peak Function from Finite Volume Kirkwood-Buff Integrals

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Volume integrals over the pair distribution function, so-called Kirkwood-Buff integrals (KBI), are a powerful tool for the thermodynamics of fluids. So far KBI has not be applied to crystalline solids, because the integrals strongly diverge when calculated in the usual way. However, when the finite volume formulation of KBI theory [1] is used, KBIs and similar integrals do converge in crystals. The Madelung energy of an ionic crystal is a mathematically subtle problem, because the lattice sum only converges conditionally. We show that the Madelung energy can be computed using finite volume KBI theory, which leads to a new real space computation method which converges unconditionally and requires neither neutral cells nor charge compensation [2]. We demonstrate that the surface contribution to the Madelung energy of spherical clusters, when averaged over possible positions of the sphere center, has a universal form, independent of ionic species and crystal structure. From this, a simple criterion for the stability of ionic clusters is derived which explains the experimentally observed structural phase transition of CsX (X=Cl,Br,I) clusters from the NaCl to the CsCl structure with increasing cluster size. Second, we show that the width and shape of Bragg peaks in powder diffraction data is given by the Fourier transform of the weight function of finite volume KBI theory [1], i.e. a geometrical function characteristic of the cluster shape . This is much simpler and more versatile than the previous calculation methods for the Bragg peak shape function.

References

[1] P. Krüger et al, J. Chem. Phys. Lett. 34, 235 (2013). [2] P. Krüger, Phys. Rev B 101, 205423 (2020).