Extension of Kirkwood-Buff Integral Theory to Solids

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Kirkwood-Buff integral (KBI) theory is a cornerstone of solution theory. While widely used for liquids, it has never been applied to crystal solids, because the integrals diverge when computed in the usual way. We show that the divergence can be avoided when employing the recently developed finite volume KBI theory [1]. We demonstrate that for perfect crystals at zero temperature, the KBIs converge to the exact, analytically known limit. This shows that KBI theory is well-defined for crystalline matter. At finite temperatures, KBIs can be computed from radial distribution functions (RDF) obtained numerically from molecular simulation. However, convergence of the integrals with system size is slow and various methods are tested for a stable extrapolation of the finite volume results to the thermodynamic limit. The theory is applied to solid Argon described by a Lennard-Jones potential. The pair-distribution function is computed with Monte-Carlo and molecular dynamics simulations in an NVT ensemble. The isothermal compressibility of Argon is calculated in the temperature range 0-70K and the experimental temperature dependence is very well reproduced. The absolute value is, however, systematically underestimated by a few ten percent. This error can be attributed to the finite-size effect of the RDF obtained from molecular simulation. Strategies to correct the RDF are discussed. Moreover we apply the theory to solid solutions and alloys and compare the results with the lattice gas models.

References

[1] Peter Krüger, Sondre K. Schnell, Dick Bedeaux, Signe Kjelstrup, Thijs J. H. Vlugt and Jean-Marc Simon, "Kirkwood-Buff Integrals for Finite Volumes",J. Phys. Chem. Lett. 4 (2013) 235-238.