Is it Possible the *ab initio* Thermodynamics with Defects?

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Phase-diagrams is considered as a starting point for materials design. Recent developments in computational thermodynamics, so called CALPHAD (CALculation of PHAse Diagram), have used to obtain the relevant phase diagrams[1]. In conventional CALPHAD techniques, the Gibbs free energies of individual phases are compared to construct the corresponding phase diagram. There is a critical problem that the current CALPHAD technique is strongly relied on the existing thermodynamic databases, which are usually assessed by experiments. The experimental thermodynamic assessments have noticed the fatal problem that a certain set of necessary thermodyanmic data is not available by experiments. For example, the solubility of silicon in cementite, which is extremely low, has been required, but the information was not able to obtain by a direct experiment for more than 30 years[2]. The experimentally unaccessible thermodynamic information can be resolved by utilizing the density functional simulations[3].

However, current density functional assessments are reliable only on the zero temperature condition. Recently, there are several challenges to deal with finite temperatures combined with the model Hamiltonians with the parameters obtained from the solutions of the Kohn-Sham equation[4]. Albeit this approach seems promising in dealing thermodynamics problem, it has at least four serious problems: First of all, the selected model Hamiltonian is rather ad hoc, so that one should answer whether the Hamiltonian is physically proper to the problem or not. Secondly, there is no physically concrete explanation on the validity of the calculated Kohn-Sham orbitals. The only physically valid Kohn-Sham orbital is the highest occupied one with the fact that the energy from the density functional theory and the density is rather close to the real particles. Thirdly, the parameters for the Hamiltonian have been obtained from the zero temperature Kohn-Sham equation. Hence, the final results contain a certain kind of scaled order parameters. Finally, the consideration of defects, which cannot be removed in any realistic materials, is obsolete with current theoretical framework..

In a structural material, the point defects, dislocations, disclinations and domain walls (grain boundaries) are important equally in determining the mechanical properties. For example, a tensile deformation is creating dislocations and it propagates. Questions have been raised long time how electronic structures and phonon structures are affected by such defects and vice versa. Brown[5] suggested to transform the Hamiltonian to adapt such defects and Teichler[6] indicated that the approach of Brown is equivalent to the gauge field theory in curved and/or twisted spacetimes. Once such defects are transformed into the Riemann-Cartan manifolds[7], the remaining task is to do calculate thermodynamic properties and the corresponding response functions within the frame work of finite temperature quantum field theory in the curved and/or twisted spacetime. They say that it began with the work of Hartle and Hawking[8] and Gibbons and Perry[9] based on the imaginary-time thermal Green's function for the description of Hawking radiation in black-hole spacetimes.

Recently, the author[10] noticed that a theoretical framework in terms of computer simulations based on an authentic ab initio thermodynamics, i.e., a fully quantum field theoretic treatments with the consideration of the

existence of defects of materials by the gauge field theory on the Riemann-Cartan manifolds is necessary for completing the phase diagram. In this study, the recent achievements of quantum field theoretic approaches with defects in terms of Riemann-Cartan manifolds are reviewed by introducing an example of spin-wave interaction with topological defects[11]. The practical aspect of such approach is going to be discussed also.

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