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Reproducibility of vibrational free energy by different methods

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ABSTRACT

The paper reviews several modern methods for calculation of Helmholtz free energy, associated with atomic vibrations: quasiharmonic approximation, self-consistent lattice dynamics method, calculation based on velocity autocorrelation function, temperature-dependent effective potential and thermodynamic integration. The results of free energy calculation by these methods are compared with each other in a wide temperature range, and their applicability is discussed. As a tool we use classical molecular dynamics modeling on the example of bcc molybdenum and fcc aluminum. The relation is observed between how the vibrational spectrum changes with temperature due to the anharmonicity of the potential and how free energy is reproduced. All methods are consistent with each other within 10 meV/at. at relatively low temperatures. At high temperatures, the discrepancy reaches tens of meV/at., although the relative error is less than 5%.

1. Introduction

Calculation of free energy is one the crucial tasks of materials science. Knowledge of free energy in various external conditions is necessary for constructing phase diagrams, determining the stability of crystal structures and defects, prediction of chemical reactions [1,2]. At this point the possibility of accurate calculation of the free energy without involving experimental data is important, since experiments in a wide range of external conditions are difficult. This question is also relevant in the development of new materials, when the criterion of phase stability should be satisfied [3].

A significant contribution to the free energy of solids is caused by thermal motion of atoms. Therefore, a method is needed that reproduces the lattice dynamics as accurately as possible. On the other hand, it must be computationally efficient, so that the calculation of free energy would not be a bottleneck, for instance, while searching for a new materials.

At present, there are many methods for lattice dynamics description and calculating free energy. They include, for example, quasi-harmonic approximation, methods of self-consistent lattice dynamics [4–6], calculation from the velocity autocorrelation function [7–9], temperature-dependent effective potential method [10–12] and thermodynamic integration method [13–16]. All of them have their pros and cons, as well as various computational cost. The present paper is devoted to a comparison of these methods, namely, how well they reproduce free energy with respect to each other. For the authors knowledge, such a complete comparison has not been made before.

As an example, the comparison was made for aluminum, as the example of fcc metal with relatively low melting temperature, and molybdenum, as the example of bcc metal with high melting point. Both of them are of importance for practical applications. As a tool, classical molecular dynamics was used. This made it possible to carry out calculations with the same accuracy for different methods, while often in the literature the results of classical and first-principle modeling are compared, as well as an experiment. The fundamental difference between these approaches introduces additional uncertainty into the comparison. The main interest here is how the results by various techniques differ under the same conditions (interatomic potential, temperature, volume).

The present paper is organized as follows. The next Section 2 is devoted to a brief description of the thermodynamic properties of a crystal at finite temperature, and a review of the methods used. Details of calculations are explained in Section 2.8. Section 3 contains the results. The discussion includes the analysis of atomic displacements (Section 3.1), the energy density of vibrational states (Section 3.2) and free energy (Section 3.3). Finally, Section 4 contains the main conclusions.

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2. Methods

2.1. Thermodynamic properties of a crystal

Helmholtz free energy F characterizes the system at a given temperature T and volume V:

$$F(V,T) \equiv \mathscr{E} - TS = \mathscr{E}_0 + \mathscr{E}_{\mathrm{vib}} - TS_{\mathrm{vib}} = F_0 + F_{\mathrm{vib}}, \tag{1}$$

where $\mathscr{E}_0$ is the internal energy of a static lattice at $T = 0$,$\mathscr{E}_{\mathrm{vib}}$ is the part of internal energy associated with thermal (including zero-point) motion of atoms, S is the entropy. By thermal motion we mean lattice vibrations, which are anharmonic in general. Restricting ourselves to classical systems, we assume that in (1) the role of electrons is reduced to an implicit contribution to the internal energy $\mathscr{E}$, and entropy is purely related to lattice vibrations. In what follows we shall consider only a part of the free energy associated with the vibrations F_{vib}.

The internal energy contains the kinetic T and the potential U part, and the latter is usually expanded in a series of atomic displacements:

$$U = U_0 + \sum_i \sum_\alpha \Phi_i^\alpha u_i^\alpha + \frac{1}{2} \sum_{ij} \sum_{\alpha\beta} \Phi_{ij}^{\alpha\beta} u_i^\alpha u_j^\beta + \frac{1}{6} \sum_{ijk} \sum_{\alpha\beta\gamma} \Phi_{ijk}^{\alpha\beta\gamma} u_i^\alpha u_j^\beta u_k^\gamma + \ldots, \tag{2}$$

Here $\mathbf{u}$ is the displacement of the ion, ijk are the atomic indices, $\alpha\beta\gamma$ are the Cartesian indexes and U_0 is the potential energy of the static lattice at $T = 0$. The second-order term corresponds to the harmonic approximation, and high-order terms are anharmonic contribution. The force constants Φ are determined by the derivatives:

$$\Phi_i^\alpha = \frac{\partial U}{\partial u_i^\alpha} = 0, \quad \Phi_{ij}^{\alpha\beta} = \frac{\partial U}{\partial u_i^\alpha \partial u_j^\beta}, \ldots \tag{3}$$

and so on.

In the harmonic approximation, the free energy can be analytically calculated. It is equal to the free energy of a system of non-interacting quantum oscillators:

$$F_{\mathrm{vib}} = \sum_\lambda \left\{ \frac{\hbar\omega_\lambda}{2} + k_B T \ln\left[1 - \exp\left(\frac{\hbar\omega_\lambda}{k_B T}\right)\right]\right\}. \tag{4}$$

Here, index λ stands for the pair of indices $(\mathbf{q},s)$ characterizing the wave vector and the polarization of the vibrational mode $\omega_s(\mathbf{q})$. The problem is that the real potential is not harmonic, and therefore different approximations are used. Using the perturbation theory [17], it can be shown that in general the anharmonicity leads to renormalization of the vibrational spectrum and its broadening:

$$\omega_\lambda(T) = \Omega_\lambda(T) + i\Gamma_\lambda(T). \tag{5}$$

The most commonly used approach is to use the renormalized frequencies $\Omega_\lambda(T)$ in (4), if the imaginary part of self-energy $\Gamma_\lambda(T)$ is low, although the accuracy of this procedure is not clear. It was shown [18,19] that in the low-order perturbation theory this is justified for entropy, but not for internal energy. In the case of strong anharmonicity the procedure is questionable.

There are a number of approaches to obtaining $\Omega_\lambda(T)$. Those used in the present work are briefly described below. Some of them require only static calculations, others require molecular dynamics (MD) simulations. One should to note, that MD gives internal energies along trajectory, but the partition function cannot be obtained directly from the simulation [20].

2.2. Small displacement method

The simplest and the most widely used method is the quasiharmonic approximation (QHA) [1,2]. Within the framework of this method, harmonic approximation is used for the potential energy (2), and the anharmonic effects are taken into account only by changing the cell volume. Within the small displacements method (SDM) the force constants $\Phi_{ij}^{\alpha\beta}$ are obtained by calculating the potential energy of the supercells with atoms displaced by a given distance $\delta = u_i^\alpha$, and frequencies of the vibrational modes are obtained by solving the eigenvalue problem.

The advantage of the method is its low computational cost and the possibility to obtain analytically all the thermodynamic properties $(F,S,\mathscr{E})$ and the spectrum of vibrational states – phonons. An obvious drawback is the unpredictability of the results if the actual potential (2) is anharmonic. In this case SDM can give incorrect results, depending on the δ, up to the dynamic instability of the system.

2.3. Self-consistent lattice dynamics method

In the method of self-consistent (*ab initio*) lattice dynamics (SCAILD) [4,21], the harmonic approximation is also assumed. However, the frequencies of the vibrational modes and ionic displacements are calculated in a self-consistent manner according to the following scheme. (i) A certain initial displacement is defined and the phonon spectrum is calculated, as described in Section 2.2. (ii) From the spectrum obtained, the atomic displacements (with zero-point contribution) at the desired temperature are analytically calculated. (iii) With these displacements new set of forces and frequencies are calculated, and then frequencies are averaged over several iterations. (iv) New displacements are calculated, using averaged frequencies. A cycle (ii)-(iv) is repeated until the convergence of the frequencies (or free energy).

SCAILD requires series of statical calculations. Typically it is tens of iteration until convergence.

2.4. Calculation of free energy from the velocity autocorrelation function

The expressions for the free energy in the harmonic approximation (4) can be written in the form of an integral over the energy (frequency):

$$F = k_B T \int_0^\infty \ln\left(2\sinh\frac{\hbar\omega}{2k_B T}\right) g(\omega)\, d\omega, \tag{6}$$

where $g(\omega)$ is the energy density of the vibrational states (VDOS), in this case the phonons. Entropy has the form:

$$S = k_B \int_0^\infty [x\coth(x) - \ln\{2\sinh(x)\}]\, g(\omega)\, d\omega, \tag{7}$$

where $x = \hbar\omega/(2k_B T)$. If the potential is not harmonic, the stationary states of the harmonic Hamiltonian are no longer exact. The realistic VDOS, with the interaction between phonons taken into account, can be obtained using MD simulation. Then this density can be used to calculate the entropy (7) or the free energy (6) in the harmonic approximation. As mentioned in Section 2.1, in the case of significant anharmonicity the applicability of such an approach is questionable.

The realistic energy density of the vibrational states can be calculated as the Fourier transform of the velocity autocorrelation function (VACF) of atoms at a given temperature [7]:

$$g(\omega) = \int_0^\infty e^{-i\omega t} \frac{\langle \mathbf{v}(t)\mathbf{v}(0)\rangle}{\langle \mathbf{v}(0)\mathbf{v}(0)\rangle} dt. \tag{8}$$

Here $\langle \ldots \rangle$ means averaging over the system. To achieve good convergence of (8), systems containing about 10^5–10^6 of atoms are required. In this regard, the method can be applied mostly with classical MD.

2.5. Temperature-dependent effective potential

Calculation of the spectrum of vibrational states at a finite temperature can be approached in a different way, using the method of temperature-dependent effective potential (TDEP) [10,11]. In the framework of TDEP a realistic potential at a finite temperature is approximated by an effective harmonic potential. To do this, for the displacements of atoms, obtained in the MD simulation, the difference