

Vibrational contribution on free energy change in binary system

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For the stability of a single phase at the finite temperatures, quasi-harmonic approximation is widely used and gives reliable predictions. In the binary systems, it is noted that the simple approximation on the configuration change for solid solution or precipitating cluster might lead the unreliable results [1].

When we assume that the free energy of single site is controlled by its vibration frequency, Taylor expansion of the free energy on the small change of frequency is expressed as

$$\Delta F = \sum_i \{f(\omega_i + \delta\omega_i) - f(\omega_i)\} \simeq \sum_i f^{(1)}(\omega_i)\delta\omega_i \simeq f^{(1)} \sum_i \delta\omega_i$$

The last equation is valid only when the first Taylor coefficient is independent on the frequency. As shown in Fig.1, it becomes fairly constant for the materials with the frequency below 10 THz and the higher temperatures. When we assume that the number and its quantity of change of softening sites are equal to those of hardening sites, the vibrational free energy change vanishes. This condition is automatically satisfied when the spring constant of the unlike-atom pair is comprised by the arithmetic mean of those of like-atom pairs, $k_{AB}=(k_{AA}+k_{BB})/2$. This too simple assumption on the spring constant is the case using the simple potential of the geometric mean, $\psi_{AB} = \sqrt{\psi_{AA}\psi_{BB}}$.

References:

1 K. Yuge, S. R. Nishitani, I. Tanaka, Calphad, 28 (2004), 167.

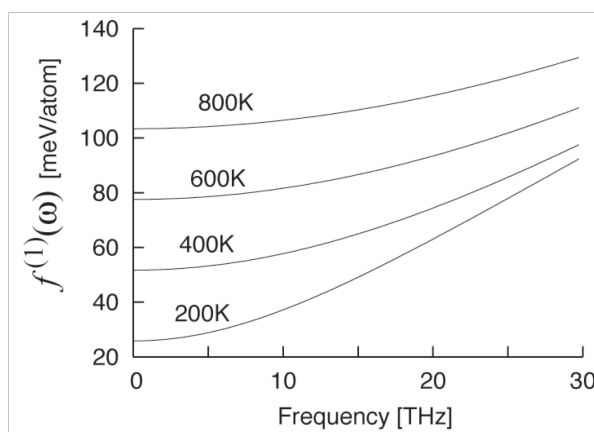


Fig.1 First Taylor coefficients as a function of vibration frequency.