STRESS-DEFECT INTERACTIONS AT MOLECULAR/CONTINUUM SCALES

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Summary External stress on a crystal affects the Gibbs free energy of formation and migration of point defects, thereby lowering/raising defect concentrations and mobilities. This effect is determined by the volume change of the crystal—for defect creation it is the formation volume, V_f. Lattice distortion *at the defect itself* can only be predicted by atomistic simulations, not by continuum elasticity. However, this distortion, represented as a dipole tensor of forces in continuum elasticity, determines the far-field deformation, and hence V_f. For the vacancy in silicon, we have quantified V_f by such studies, using the Stillinger-Weber empirical potential at atomic scales and elasticity at continuum scales. We also have treated issues related to bridging these scales, obtained consistent interpretations of parameters, identified the limitations of continuum, molecular and *ab initio* calculations, and found overall agreement with relevant results by Eshelby.

BACKGROUND

Point defect (vacancy/interstitial) concentrations are determined by their Gibbs free energies of formation, G_f. The influence of an *external stress*, $\boldsymbol{\sigma}$, is to raise or lower G_f. For mobile defects, this modulation is apparent also on the migration energy. Consequently, the concentration and mobility of point defects are strongly influenced by $\boldsymbol{\sigma}$. Solid state diffusion of dopant atoms in silicon and germanium requires pairing of these atoms with mobile point defects. Therefore, it is presently of great technological importance to understand the interaction mechanism between external stress and defects. A formation volume, V_f, quantifies the interaction and is entirely determined by deformation of the crystal around the point defect (following section). Continuum elasticity cannot predict the distortion at the defect itself; this field must be extracted from atomistic calculations. For vacancies/interstitials the distortion at this scale is strongly influenced by changes in bonding between first- and second-nearest neighbor atoms. The accuracy of *ab initio* calculations [1] notwithstanding, this class of methods may not be ideal for determining the overall crystal deformation, and hence V_f: While values of V_f converge only for systems much larger than 500 atoms, *ab initio* calculations are currently limited to about 500 atoms, placing larger systems beyond the present reach of these methods.

Molecular simulations allow system sizes that, at millions of atoms, are larger by many orders of magnitude. Realistic crystal sizes are still not attained, but the systems are large enough that displacement and stress fields escape the effect of lattice discreteness at the point defect. Most importantly, they converge to the elastic fields which, when appropriately scaled, are invariant of crystal size. We have carried out such atomistic calculations of the mono-vacancy in silicon using the Stillinger-Weber interatomic potential. If the deformation at the defect is represented as a dipole tensor, continuum elasticity solutions of the displacement and internal stress fields can be obtained using the Green's function for anisotropic elasticity. These fields are indispensable for checking the far-field solutions from atomistic calculations. In turn, far-field solutions determine V_f.

ELASTICITY AND MOLECULAR STUDIES OF VACANCY-INDUCED DEFORMATION

The dipole tensor (preceding section), $\boldsymbol{D}$, used as the continuum elasticity analogue of a vacancy, is called a center of contraction. The displacement and internal stress fields around a vacancy can be obtained by using the Green's function for anisotropic elasticity [3]. The body force in the Green's function method is specified by $\boldsymbol{D}$. Being a continuum representation of the forces on nearest-neighbor atoms of the vacancy, $\boldsymbol{D}$ must be extracted from molecular calculations. An accurate quantification of $\boldsymbol{D}$ thus determines the deformation field and hence V_f. Any method to obtain $\boldsymbol{D}$ essentially imposes consistency between the fine scale atomistic calculations and "coarse scale" continuum elasticity for this problem.

Employing the Stillinger-Weber interatomic potential for silicon, the dipole tensor, $\boldsymbol{D}$, was obtained by a least squares' minimization of difference between interatomic forces from the molecular calculations, and the elasticity solution for force at the same point due to the vacancy as center of contraction. For ease of writing we describe this functional using the isotropic elasticity solution in an infinite medium:

$$\mathcal{F} = \sum_{i}^{n_\mathrm{atom}} \left| \boldsymbol{f}_i - \frac{\mu\, \boldsymbol{D}\boldsymbol{r}_i}{\pi(\lambda+2\mu)|\boldsymbol{r}_i|^4} \mathrm{d}A_i \right|^2 . \tag{1}$$

Here, n_atom is the total number of atoms, $\boldsymbol{f}_i$ is the force on the i^th atom, $\boldsymbol{r}_i$ is the position vector of the atom relative to the vacancy, λ and μ are the Lamé parameters of the isotropic medium, and $\mathrm{d}A_i$ is the radial projection of the atom's cross-sectional area. The necessary condition for minimization of $\mathcal{F}$ with respect to $\boldsymbol{D}$ gives a closed-form result for the dipole tensor. Assuming a dipole tensor of the form $\boldsymbol{D} = D\mathbf{1}$, where $\mathbf{1}$ is the second-order isotropic tensor, the extracted value of D is found to vary as explained in Figure 1.

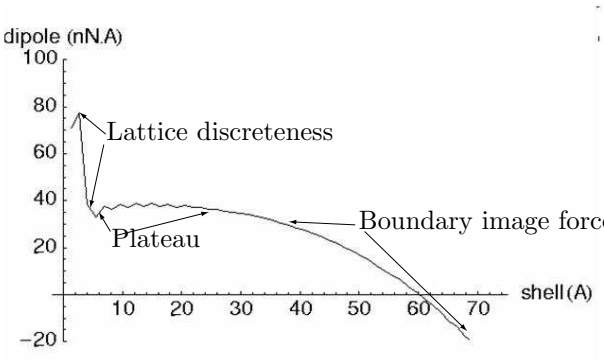

Figure 1. Atomistic calculations for variation in D with radial position of shell of atoms used to extract it. (i) Discreteness effect: Continuum elasticity does not hold close to the vacancy; the discreteness of the lattice dominates the results here. (ii) Plateau: In a range sufficiently far from the vacancy, continuum elasticity holds, and as it predicts, D is essentially constant. (iii) Boundary image force: For a finite computational cell of atoms, image forces from the periodic boundaries exert their influence. Therefore, D fitted to the exact elasticity result for an infinite crystal deviates from the expected constant value.

Our detailed calculations use the anisotropic elasticity solution for a *finite crystal*, in which case D is more nearly constant as the free boundary is approached. The important result, that $D \approx 38\,\mathrm{nN}\cdot\mathrm{\AA}$ holds.
As a check for consistency the extracted dipole value was used in continuum elasticity calculations on an anisotropic silicon crystal, of finite extent, and cubic in shape. The relaxation volume measured at the crystal free surface is independent of the crystal size, as can be understood by considering the case of the isotropic, spherically-shaped crystal of radius R:

$$V(r) = \frac{D}{\lambda + 2\mu}\left(1 + \frac{4\mu}{3\lambda + 2\mu}\left(\frac{r}{R}\right)^3\right). \tag{2}$$

For a crystal of any radius, $V(R) = \frac{D}{\lambda+2\mu}(1 + \frac{4\mu}{3\lambda+2\mu})$ is independent of R. For anisotropic finite crystals of cubic shape, finite element calculations resulted in a relaxation volume $\approx 30\,\mathrm{\AA}^3$. This is in reasonably good agreement with the relaxation volume of $\approx 34\,\mathrm{\AA}^3$ obtained directly from the molecular calculations (Figure 2).

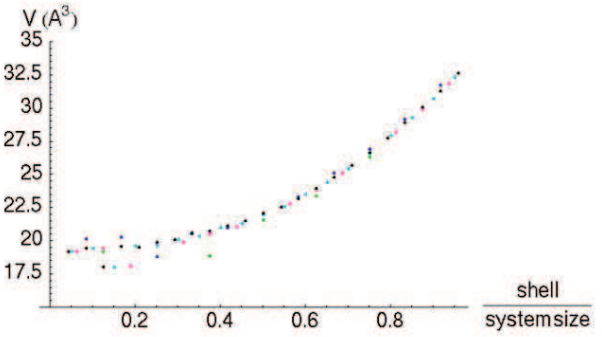

Figure 2. Variation of relaxation volume with r/L from molecular calculations on cubic computational cells of side $2L$.

A final question that arises is whether the internal volume, $V(0)$ in (2), or the external volume, $V(R)$ is the thermodynamically-appropriate formation volume that is conjugate to an external stress. In other words, under a uniform external stress, $\boldsymbol{\sigma} = p\mathbf{1}$, when the stress-free Gibbs free energy G_f^0 is modified to $G_\mathrm{f} = G_\mathrm{f}^0 - pV_\mathrm{f}$, is $V_\mathrm{f} = V(0)$ or $V(R)$? Eshelby [2] shows that for a continuum body, when a sub-domain undergoes a *stress-free* reduction in volume ΔV, the work done by p is $p\Delta V$. It is not immediately obvious how this result can be applied to the present case, since here the sub-domain is the defect, which is discrete, and does not admit the continuum arguments used by Eshelby. Also, it is unclear what the stress-free reduction in volume is at the defect, and how it is related to $V(0)$ and $V(R)$. We have devised a construction in the spirit of Eshelby's "cutting and welding" operations which shows conclusively that $V_\mathrm{f} = V(R)$ is conjugate to $\boldsymbol{\sigma}$. Thus $G_\mathrm{f} = G_\mathrm{f}^0 - pV(R)$ is the correct Gibbs free energy of formation under external stress.

CONCLUSION

We have consistently combined continuum elastic and atomistic calculations to answer fundamental questions on the thermodynamics of point defect formation under stress. By our calculations we have arrived upon a deformation field that is consistent between atomistic and continuum methods, and yields the vacancy formation volume. Notably, the result is in agreement with the stress-defect interaction result of Eshelby [2]. Our methods will be used to study the thermodynamics of vacancy migration, and the formation/migration of the interstitial and dopant-defect pairs.

References

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