Free energy barrier for the migration of a vacancy in copper crystal

The project proposed initially aimed at the implementation of computational techniques for estimating the free-energy barrier for phase separating binary liquid mixtures. However, given the limited duration of the visit (3 months), a simpler study case was better fitting the need. It has been agreed that the free-energy barrier opposing the vacancy motion in crystals fulfilled this requirement.

Crystalline copper is conveniently modeled via phenomenological potentials deriving from the second moment approximation of the tight-binding scheme[1]. Such a potential was chosen for this work and the migration energy of the vacancy at T=0 K has been determined via the nudged elastic band technique[2]. The calculations yield the value, E_m=0.71 eV, in good agreement with the experiment (E_m=0.7[3]-0.8[4] eV). The next step consisted in the implementation of the string method[5] in collective variables combined with the evaluation of the mean force[6] acting on an atom migrating toward the vacancy in a isobaric-canonical Monte Carlo code. The results obtained thereby are shown in the figure below and are compared with the derivative of the migration barrier at T=0 K with respect to the reaction coordinate. It can be seen that at T=300 K, the mean force profile differs very little from its counterpart at T=0 K. This is consistent with the modest value of the entropy associated with the vacancy migration reported in the literature[7], $S_m \approx 1\text{-}2\ k_B$.

Ongoing work is focusing on the objectives of the initial project.

During this stay, work in progress on capillary waves in interfaces between immiscible liquids has benefited from fruitful discussions with the ACAM staff members and has been finalized[8]. The European Science Foundation and SimBioMa are warmly acknowledged for the granted financial support.

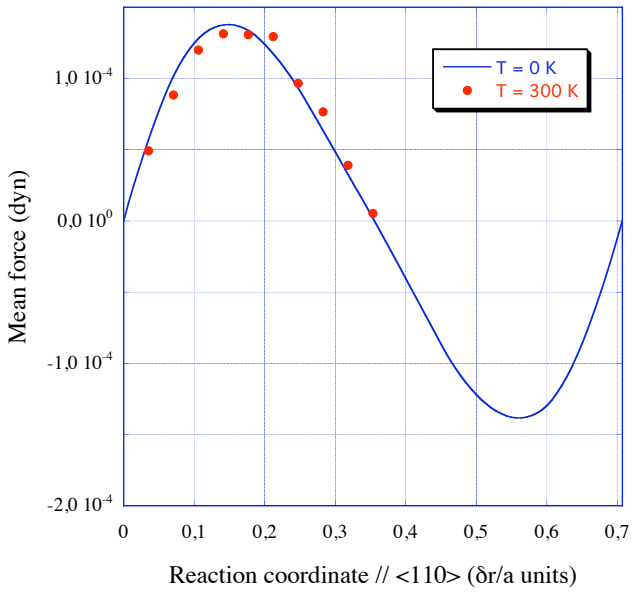

Figure 1 – Mean force acting on a atom migrating toward a vacancy at a first neighbor position: T = 300 K (full dots) and force profile computed at T=0 K using the nudged elastic band technique (full line).

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