

Ab initio Molecular Dynamics and Elastic Properties of TiC and TiN Nanoparticles

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ABSTRACT

The results of first-principles simulations of relaxed ground-state structure and vibrational modes are presented for titanium carbide and titanium nitride clusters of nearly stoichiometric composition and compared to frozen phonon and molecular dynamics calculations for crystalline TiC and TiN. The calculations have been done with the SIESTA method, using norm-conserving pseudopotentials and the basis of strictly localized numerical pseudoatomic orbitals. The dominant vibration mode corresponding to the zone-center TO phonon (14 THz) persists and gets hardened (21 THz) in the small Ti_4C_4 cluster. The increase of the cluster size to $\text{Ti}_{14}\text{C}_{13}$ leads to an enhancement of vibrational density of states in the intermediate range of frequencies, including the phonon band gap of pure crystalline TiC (near 15 THz). Similar trends can be noted for the Ti-N system, with the vibration spectrum slightly scaled upwards but otherwise very close to that of TiC. The clusters studied are yet too small to perform a reliable analysis of acoustic modes.

INTRODUCTION

Titanium carbide and nitride prepared as nanoparticles find many applications. Among their peculiar properties different from those in the bulk phase, a considerable softness could be expected. Elastic properties of nanoparticles are difficult to access in direct experimental measurements, but hopefully due to their relation with electronic structure they can be reasonably estimated from first-principles calculations, as is known to be the case for many crystalline materials. The meaning of strain or homogeneous external pressure may not be so straightforward in a computational experiment on small clusters as it is for bulk crystals. However, different vibrational modes may be induced in a simulation and give a clue e.g. of the sound velocity in nanoparticles. For a detailed analysis it is advantageous to have accumulated data from sufficiently long molecular dynamics (MD) simulations, that would permit to project out various modes of interest, with respect to their frequency and/or wavenumber, and reconstruct the vibrational density of states. The present study is a preliminary attempt towards such analysis, where we present data on very small TiC and TiN particles and concentrate on their quite general vibrational behavior, as compared to that in corresponding bulk systems.

CALCULATION METHOD

The central element in first-principle calculations of vibration frequencies and patterns is a reliable and precision method to extract total energy and/or forces for any distorted (e.g., low-symmetric) configuration of a system of interest. (Linear response schemes that provide directly dynamical matrices without actually displacing the atoms may provide a more elegant, albeit

methodically much more involved, alternative - see Ref.[1] for a recent review). In the present study, we used the SIESTA method [2] that is based on density functional theory and employs a compact and efficient basis of numerical functions (pseudatomic orbitals). Norm-conserving pseudopotentials are used for excluding core states from an explicit calculation. Since the basis set is not a plane-wave one, the use of (possibly hard) norm-conserving pseudopotentials does not necessarily pose a problem. The electrostatic (Hartree) and exchange-correlations potentials include contributions from the slowly varying difference charge density (of general form) calculated on a three-dimensional real-space grid. A single energy cutoff parameter defines the step of this grid and hence the numerical accuracy of the density representation. Specifically, we used the Troullier-Martins pseudopotentials [3] generated for the following electronic configurations: $Ti3p^63d^{2.5}4s$, $C2s^22p^2$, $N2s^22p^3$. Double-zeta basis set with polarization orbitals was used. The energy cutoff of 200 Ry (resulting in 40 grid divisions along the rocksalt lattice parameter) was found sufficient for the TiC systems, somehow denser grid corresponding to the cutoff of 300 Ry was needed for the TiN systems, due to stronger localization of the $2s$ orbital. The calculations for crystalline (and stoichiometric) TiC and TiN have been done in the rocksalt structure, considering the primitive fcc cell (for calculation of elastic properties and the Γ -phonon), as well as for a quadrupled (cubic) supercell for the simplest test case of MD in the bulk. The finite clusters we considered were genetically cubic fragments Ti_4C_4 and $Ti_{14}C_{13}$ (and similarly for the TiN composition), first relaxed and then subject to MD simulations. Several larger TiC clusters have been studied in conjugate-gradient optimizations of structure, but so far without accessing their dynamic properties. Although basis functions are atom-centered and strictly localized, a simulation cell (large enough to avoid the overlap of basis functions across the cell boundary) has to be introduced in the SIESTA method in order to be able to solve the Poisson equation by fast Fourier transform. The edge of (cubic) simulation cells were 24 a.u. for Ti_4C_4 and 30 a.u. for $Ti_{14}C_{13}$.

ELASTIC PROPERTIES AND ZONE-CENTER PHONONS IN PERFECT CRYSTALS FROM FIRST-PRINCIPLES CALCULATIONS

Electronic structure and lattice dynamics of titanium carbide has been subject to many previous studies. Ground-state electronic structure in the ordered phase along with elastic constants have been addressed in a precision total-energy calculation (for TiC, TiN and TiO) [4]. Previous calculations of just electronic structure in ideal and in non-stoichiometric crystals, as well in clusters of different size and geometry, are very numerous; dynamical properties are much less studied. For ordered crystals, phonon dispersion curves are quite well known from experiment [5] and have been reproduced with reasonable accuracy in recent calculations [6] using the total-energy pseudopotential code for extracting force constants. For TiN, we are not aware of any similar calculations. It is relatively easy to calculate the frequency of the zone-center phonon in the rocksalt structure. We did corresponding estimates using the total energy vs. displacements based on the total-energy calculations by the full-potential linearized augmented plane wave method [7]. These results served primarily as benchmark for the similar, but much faster, frozen-phonon calculations done with the SIESTA method, incorporating, differently from the full-potential LAPW scheme, norm-conserving pseudopotentials and compact basis set consisting of numerical strictly localized functions. The advantage of SIESTA is its applicability

Table I. Equilibrium lattice constant a , bulk modulus B and Γ -TO phonon frequency ν in TiC and TiN from experiment and theory.

a (a.u.)	B (Mbar)	ν (THz)	
TiC			
8.159	2.4	16.3	Exp. [5]
8.037	2.7		Ref. [4] (FP-LMTO, LDA)
8.153	2.2		Ref. [4] (FP-LMTO, GGA)
8.069	2.96		our results (WIEN97, LDA)
8.064	2.75	14.2	our results (SIESTA, LDA)
8.183	2.53	13.6	our results (SIESTA, GGA)
TiN			
8.013	3.2	15.9	Exp. [8]
7.863	3.1		Ref. [4] (FP-LMTO, LDA)
7.994	2.7		Ref. [4] (FP-LMTO, GGA)
7.907	3.32		our results (WIEN97, LDA)
7.901	2.98	13.9	our results (SIESTA, LDA)
8.076	2.47		our results (SIESTA, GGA)

to large and low-symmetric systems, that allows us to perform the MD study described below. The results of frozen-phonon calculations are summarized in Table I.

RELAXED STRUCTURE OF SMALL CLUSTERS

The smallest (stoichiometric) clusters we considered represented the "cubic" fragment, slightly distorted in the course of the static relaxation, yielding the interatomic distances as shown in Table II. The $\text{Ti}_{14}\text{C}_{13}$ composition is being found in abundance in the course of experimental creation of small titanium carbide clusters, and the $3\times 3\times 3$ fcc structure seems the plausible one for it (see Ref. [9] for a review). Moreover, we optimized the structure of larger clusters $\text{Ti}_{16}\text{C}_{16}$ and $\text{Ti}_{20}\text{C}_{20}$ that include a further (uncomplete) shell of neighbors, differently terminated, around the "prototype" Ti_4C_4 cube. The universal trend in the relaxation is a surface contraction in all cases, slightly larger for the C atoms than for Ti, and nearly stabilization towards the bulk interatomic distances inside the cluster. More details about these larger relaxed clusters, along with dynamical simulations for them, will be given elsewhere.

Table II. Distances of atoms R (Å) from the center of masses in relaxed Ti_4X_4 and $\text{Ti}_{14}X_{13}$ clusters ($X = \text{C}, \text{N}$) in comparison with corresponding distances in perfect crystals (in brackets).

Cluster	R (Ti)	R (X)
Ti_4C_4	1.672 (1.847)	1.668 (1.847)
$\text{Ti}_{14}\text{C}_{13}$	2.042 (2.133) 3.403 (3.695)	2.957 (3.017)
Ti_4N_4	1.665 (1.850)	1.599 (1.850)

MOLECULAR DYNAMICS SIMULATIONS

Ab initio MD studies accumulate information about trajectories of individual atoms in coordinate and velocity space and thus allow to calculate the velocity autocorrelation function [10]. The Fourier spectral density of the latter gives the vibrational density of states. Differently from the frozen phonon approach, this analysis automatically incorporates anharmonic effects, possibly with a temperature imposed as a parameter of simulation (via introducing an appropriate thermostat, if the system is reasonably large). Moreover, a more detailed analysis of various partial correlations of interest is available, once the trajectories are accumulated. The main disadvantage is the necessity to perform a simulation for sufficiently large number of steps, in order to go beyond the initial step of equilibrating the system and to achieve good resolution of the resulting spectrum in the frequency domain. Moreover, in a simulation of a periodic system the number of atoms in a simulation box (i.e., supercell) should be large enough in order to ensure that reasonably large portion of the global phase space of the system will be visited in the course of simulation.

In dynamical simulation of finite-size particles the latter aspect is of no special importance because the size of the system is anyway the same as in the frozen phonon calculation, and all vibrations are "zone-center" ones, i.e. there is no phonon dispersion and simply a sequence of discrete vibration frequencies. However, as the number of atoms grows, the MD approach starts to gain in attractivity versus the frozen phonon one: in the latter, one has to collect information (i.e., forces on all atoms in the system) from a large set of trial calculations, say for 7 displacements of each atom, in order to construct dynamical matrix, and frequencies become available only after diagonalizing the latter. In the MD simulation, the main features in the vibration spectrum emerge already after relatively few (say, several hundreds) of simulation steps and become gradually refined in the course of longer MD run.

Whereas the estimation of elastic properties, e.g., velocity of sound in a particle, seems problematic in a frozen phonon calculation with no phonon dispersion explicitly available, some estimations in the MD simulation can be done based on the analysis of velocity autocorrelation functions, or from the shape of the vibration density of states.

With this in mind, we performed MD simulations on small TiC and TiN clusters introduced in the previous section and compare them with the bulk supercell calculations of corresponding perfect crystals. For the periodic crystals, the simulations have been done for a (relatively small) supercell of 8 atoms, chosen for a better comparison with finite cluster results. One should note that such relatively small supercell allows sampling over zone-center and zone-boundary phonons only and only approximately represents the density of states summed up over the full Brillouin zone that can be found, e.g., in Ref. [6] for TiC.

The vibrational densities of states are shown in Fig. 1. For bulk, the dominant peak at 19 THz originates from the optical branch and is shifted to higher frequency, as compared to the frozen-phonon result, due to the phonon dispersion (upwards from the minimum at the Brillouin zone center). The fine structure of this peak, which according to both experiment [5] and phonon density calculation [6] consists of two maxima shifted apart by ~ 4 THz, is almost absent in our calculation, because the L TO mode, for which the splitting between two optical branches is maximal, is not sampled in our supercell. On the contrary, the X phonons may be induced in the MD simulation, and the splitting of the acoustic branches around 10 THz at the Brillouin zone boundary is perfectly represented by two well resolved peaks in the vibrational density of states.

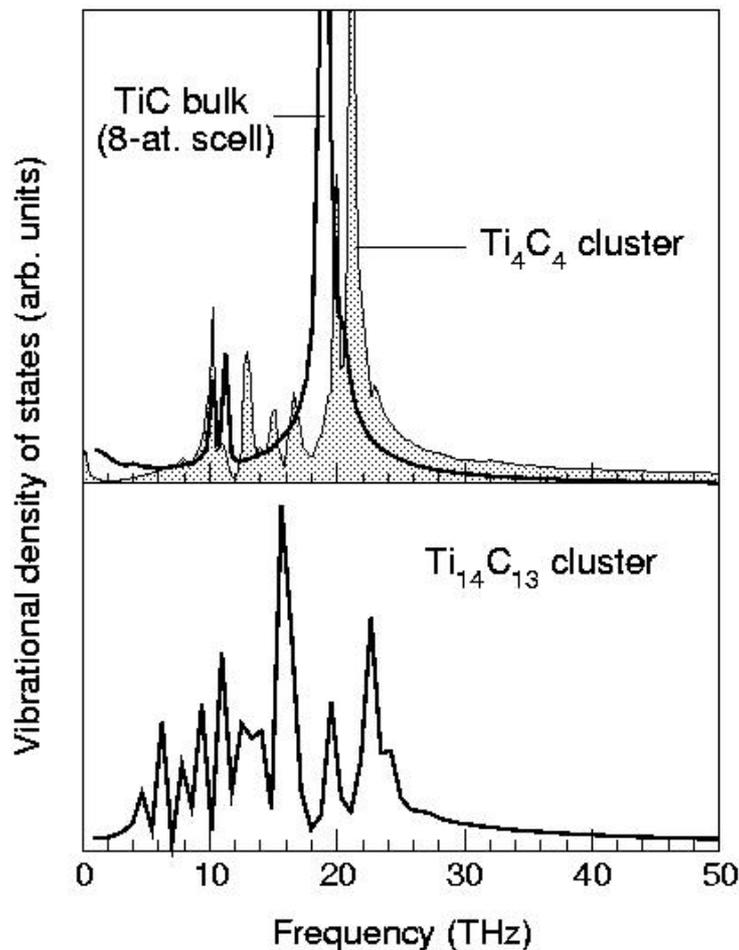


Figure 1. Vibrational density of states as extracted from ab initio MD simulations for bulk TiC (8-atom supercell, thick line in the top panel), Ti₄C₄ cluster (shaded area in the top panel) and the Ti₁₄C₁₃ cluster (bottom panel).

The vibrational density of states of the Ti_4C_4 cluster is of the same general shape, but shows more features, due to the lower symmetry as compared to the crystalline case. A family of well resolved peaks appears in the region 10 to 20 THz, covering also the gap in the phonon spectrum of bulk TiC near 15 THz. The hardest vibration line is associated to the motion of two interpenetrating Ti_4 and C_4 tetrahedra, "breathing" in antiphase. As compared to the corresponding TO mode in the bulk which describes the relative displacement of two sublattices, its frequency is enhanced as a consequence of reduced coordination number on the surface.

The intensity in the vibration spectrum of the $\text{Ti}_{14}\text{C}_{13}$ cluster drops down at slightly higher frequency (near 24 THz) than in Ti_4C_4 . One can see that the upper part of the spectrum, with two dominant features at 16 and 23 THz, starts to recover two-peaked structure of the optical band in crystal [5,6]. Differently from the case of bulk TiC, the phonon bandgap is not pronounced, and the low-frequency part of the vibrational density is not smooth enough to reliably extract information related to acoustic waves. The vibrational density of states shown in Fig.2, bottom corresponds to only 880 steps (of 2.5 fs) of the MD simulation. A longer MD run would result in better resolved spectra features. Also, the analysis of larger clusters would facilitate the analysis of the acoustic part of the phonon spectrum.

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