FROM ELECTRONIC STRUCTURE TO THERMODYNAMICS

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ABSTRACT

A simple way to extend the remarkable results of Density Functional calculations to finite-temperature properties of materials is the quasi-harmonic theory of Lattice Dynamics. In this framework a thermodynamically consistent theory needs the complete phonon spectrum for a large periodic system (30-100 atoms/cell) at many different volumes, which poses severe practical limitations. In this paper I present the application to a semiconducting system of a method recently proposed by Bachelet and De Lorenzi to overcome these limitations. Based on low-temperature Molecular-Dynamics trajectories (now possible from first principles for semiconducting systems according to the method of Car and Parrinello), the method is shown to provide accurate dynamical matrices for an 8-atom silicon supercell. Such a successful, preliminary test, together with the fact that for larger and/or lower-symmetry systems the computational effort required by the "trajectory approach" is lower than traditional frozen-phonon or force-constant techniques, suggests its use in the determination of dynamical matrices of larger defect or amorphous systems, and thus in the study of their thermodynamics from first principles.

INTRODUCTION

Over the last ten years the theory of lattice defects and impurities in semiconductors has evolved from empirical descriptions, aimed at the interpretation of their optical levels in the fundamental gap, to the ability of predicting from first principles their equilibrium atomic geometry and the structural energies associated to selected saddle-point geometries at zero temperature [1]. Key ingredients of such a growth were the Density Functional (DF) Theory of Hohenberg, Kohn and Sham [2], the simultaneous development of new, general band-structure methods [3-5], and finally specific computational techniques conceived for the deep-center problem [6-10]. The success and reliability of DF calculations (in the Local Density approximation) for bulk semiconductors [11] has encouraged many groups to use the same tools to study the properties of defects in semiconductors; over the last five years DF results in remarkable agreement with each other were obtained for benchmark systems (like the silicon vacancy) using widely different computational techniques (e.g. Green's function and supercell). This effort also produced important contributions for the study of defect migration in semiconductors, within the limits of a zero-temperature theory [10,12,13]. At this stage one can begin to face the appealing challenge of predicting finite-temperature thermodynamical properties of semiconducting systems, like bulk thermal expansion, or free energies of formation and migration of defects, or thermodynamics of amorphous semiconductors.

LATTICE DYNAMICS AND MOLECULAR DYNAMICS

Quasi-harmonic Lattice Dynamics deserves to be considered as a good candidate for this purpose: from the knowledge of total potential energy, phonon frequencies and some of their derivatives with respect to volume (all quantities which can be obtained from more or less laborious state-of-art Density Functional calculations for perfect and imperfect crystals) it is possible to extract the thermodynamical quantities of interest [14]. Quasi-harmonic Lattice Dynamics (QH-LD), where anharmonicity is partially incorporated through the volume dependence of phonon frequencies, is expected to work well for semiconductors: even Lennard-Jones systems, which exhibit much stronger anharmonicity than semiconductors, are described fairly well by such a theory [15]. Its application requires the accurate evaluation of the determinant of the dynamical matrix as a function of volume, or, if quantum effects are significant (i.e. at very low temperature) the evaluation of individual phonon frequencies vs. volume, in the equilibrium atomic configuration of the system under consideration. With these inputs one then uses the expression of the

Helmholtz free energy F and the internal energy U in the harmonic approximation:

$$F = E_o + \frac{1}{2} \sum_{n=1}^{3N-3} h\nu_n + k_B T \sum_{n=1}^{3N-3} \ln \left[1 - \exp\left(- \frac{h\nu_n}{k_B T} \right) \right] \quad (1)$$

$$U = E_o + \frac{1}{2} \sum_{n=1}^{3N-3} h\nu_n + \sum_{n=1}^{3N-3} \frac{h\nu_n}{\left[\exp\left(\frac{h\nu_n}{k_B T} \right) - 1 \right]} \quad (2)$$

E_o is the total potential energy. The normal mode frequencies ν_n are simply related to the eigenvalues of the dynamical matrix. Having in mind an N-atom crystal with periodic boundary conditions (i.e., the supercell geometry) one sees that the three translational degrees of freedom of the center of mass have been excluded from the sums. Other relevant quantities are the entropy $S = (U - F)/T$ and the pressure $P = -(\partial F/\partial V)_T$. If the eigenfrequencies ν_n are not allowed to change with volume, then the purely harmonic description is recovered: pressure does not depend on temperature and important effects like the thermal expansion, entirely due to anharmonic effects, disappear. Including the volume dependence of normal mode frequencies amounts to the quasi-harmonic theory. It preserves many important physical consequences of anharmonicity like e.g. thermal expansion and temperature-dependent elastic constants.’ Its use in the study of thermodynamical properties of defects as well as its limitations have been widely discussed in the literature [14]. Of course, by including only phonon effects in the free energy, one implicitly disregards the contribution of thermal electronic excitations to the finite-temperature properties. Such an effect should be negligible in the bulk at temperatures well below the melting point (as indirectly shown by the results of Ref.16). An appropriate treatment of this effect may be required for defects with multiple charge states in the gap [17], but even then the phonon contribution will have to be accounted for.

After the advent of the new unified approach of Molecular Dynamics and Density Functional Theory [18] not only the statics, but also the dynamics of semiconductor systems can be studied from first principles at the atomic level. This suggests that finite-temperature thermodynamical properties of perfect and imperfect semiconductors may be attacked from a different side, namely, via Molecular Dynamics (MD) studies. In this case one would sample configurations and evaluate thermal averages related to free energies. Such an approach is exact with respect to anharmonic effects, but, as far as defects are concerned, its statistical character represents a drawback for the evaluation of free energy differences as e.g. the free energy of formation of a point defect. If N is the number of atoms in the crystal, point defects contribute only terms of order 1/N to the total crystal properties, so that in standard MD calculations the sought result is buried in the statistical noise [15]. Moreover the knowledge of the full dynamical matrix vs. volume contains more detailed information (like e.g. eigenvectors), which may in some circumstances be of great interest for the understanding of the physical system under examination [19]; another advantage of QH-LD over the use of MD is the possibility of including quantum effects at very low temperature.

LATTICE DYNAMICS FOR BULK AND VACANCY IN SILICON

There has been a recent attempt to use QH-LD formulas in connection with Density Functional force and total energy calculations [20], with two goals: the calculation of the lattice thermal expansion of bulk silicon and the calculation of the free energy of formation at constant lattice parameter of the silicon vacancy in the doubly positively charged state. A very small unit cell (N=8 atoms) with periodic boundary conditions was employed. The two main results were: (1) the bulk crystal with eight atoms/cell was already able, within QH-LD, to give meaningful results in good qualitative agreement with the experimental thermal expansion of silicon; in particular to reproduce the peculiar feature of low-temperature negative thermal expansion coefficient of this material, a typical quantum effect due to the negative Grüneisen parameter of the TA phonon [21]; (2) the calculated free energy of formation as well as the entropy of formation at constant lattice parameter of the double-plus vacancy, whose calculation from first principles had never been attempted before, turned out to be also reasonable, compared to available experimental and theoretical estimates. The vacancy calculation implied a considerable additional effort: for 5-10 different lattice constant around the experimental silicon value it was necessary first to find the relaxed equilibrium configuration of the double plus vacancy; then to perform a number of additional calculations for ionic configurations slightly displaced from this minimum to get the dynamical matrix for that volume, as already done for the bulk. The numbers obtained - an entropy of formation around $3k_B$ and a rather weak dependence on temperature of the free energy of formation at constant lattice parameter - were in good agreement with the valence force model of Lannoo and Allan [22] and compatible with the experimental estimate of Dannefaer [23] for the neutral vacancy, for which a larger entropy is expected because of the Jahn-Teller relaxation. But N=8 atoms was too small for a thermodynamically consistent theory (one is clearly too far from any reasonable approximation of the thermodynamic limit; in any event the only convincing test would have been the stability of calculated thermodynamic quantities for cells of increasing size). Being the first attempt in this direction, such an outcome was nonetheless encouraging, and clearly suggested that it was worth trying to apply this method to a more complete study based on larger unit cells and aimed at the study of the formation and migration free energies of the vacancy in its different charge states. At the same time experience on the small supercell taught that such a task would have been, for medium-large supercells (30-100 atoms), rather exhausting, since it would imply, for each of the 5-10 volumes considered and low symmetry systems like the fully relaxed vacancy, a tremendous amount of both human and computer time in working out a high number of configurations slightly displaced from equilibrium (both for the bulk and for the various charge states of the vacancy), each of which needed an independent self-consistent calculation. So it seemed that unless more economic and "automatic" (yet equally accurate) prescriptions were conceived to determine dynamical matrices from first-principles LDA calculations, the need of larger supercells would remain unsatisfied.

A NEW USE OF MOLECULAR-DYNAMICS TRAJECTORIES

In this spirit a totally different way of taking advantage of MD trajectories was recently proposed [24], based on two simple ideas: (a) at very low temperature anharmonic effects become vanishingly small, and the force-displacement relation of a many-body system becomes a linear one, and (b) physical trajectories of a many-body system are a good way of generating sets of independent displacements and corresponding forces, from which the dynamical matrix of the system is obtained using standard tools of linear algebra. Such an approach has a remarkable feature. In most physical theories the existence of symmetry reduces the computational effort required for its numerical implementation; the use of trajectories, instead, becomes more and more efficient as the symmetry of the system becomes lower and lower. A key observation of Ref.24 is that in a 3N-dimensional harmonic oscillator the presence of symmetries (i.e. degeneracies in the eigenvalue spectrum) forces an individual physical trajectory to lie in a subspace of lower dimensionality than 3N, and thus to contain less information than required to build up the dynamical matrix; the lower the symmetry of the system, the higher the dimension of the subspace where an individual trajectory lies; until, in the complete absence of symmetry, a single physical trajectory will belong to the full 3N-dimensional space, and thus contain all the information required to build up in one shot the dynamical matrix. This is easily understood as the 3N-dimensional generalization of a well known 3D case: it is generally possible (apart from "pathological" initial conditions, which are easily identified) to pick up three linearly independent position and force vectors from a single physical trajectory of an **anisotropic** 3D harmonic oscillator; on the contrary, for a spherically **isotropic** harmonic oscillator, angular-momentum conservation due to central symmetry implies that an individual physical trajectory always lies on a plane, so that no more than two linearly independent vectors can be extracted from it. The generalization of this known effect to the 3N-dimensional case was worked out in Ref.24; there it was also determined, if one trajectory is not enough because of the high symmetry of the system considered, how many of them (with independent initial conditions) are required to get complete information about its dynamical matrix. As we see the relation between trajectories and degeneracies makes their use most efficient for systems of lowest symmetry (like relaxed defects or amorphous materials). We also observe that the number of trajectories required to build up the dynamical matrix for symmetric systems does not depend on the size of the system, but only on its maximum degeneracy, and is typically small even for highly symmetric cases.

For example, excellent results were obtained with 10 low-temperature trajectories and random initial conditions by Bachelet and De Lorenzi for a 32-atom argon crystal with and without a relaxed vacancy, for which exact results are available (the potential energy is the sum of pair potentials). Their results are reproduced in Fig.1 and Table I.

Of course the use of trajectories was conceived - and becomes really convenient - for semiconducting systems: on one hand the second derivatives of the total potential energy are not directly available from self-consistent calculations; on the other, Molecular-Dynamics trajectories can be generated from first-principles LDA calculations in a relatively economic way [18]. If we succeed and produce in this new way dynamical matrices for low-symmetry, large size semiconducting systems, we can then feed them back into QH-LD theory and get thermodynamical quantities of interest.

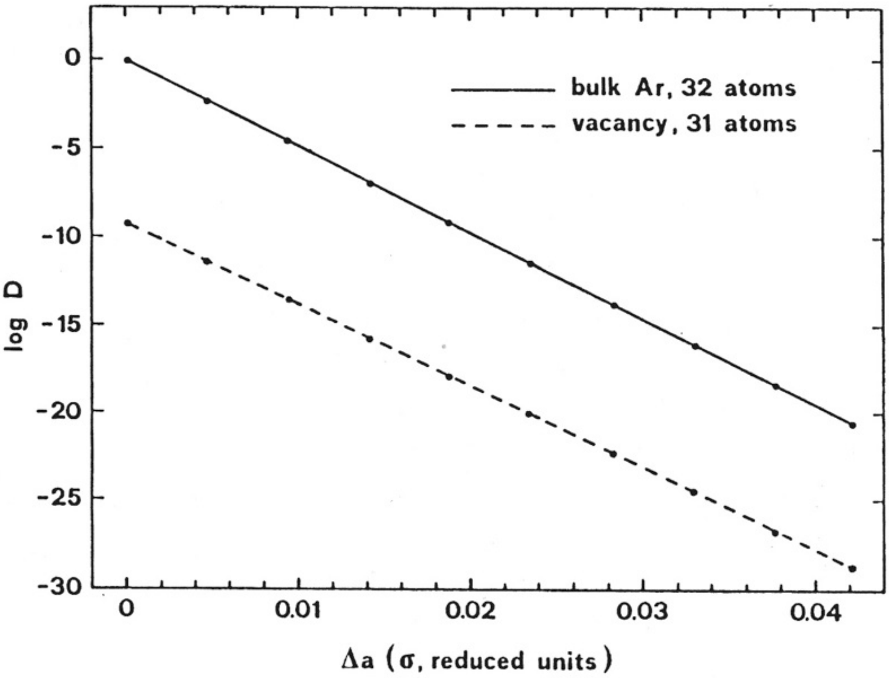

Fig. 1 Determinant of the dynamical matrix vs. lattice parameter in argon reduced units. Solid: bulk. Dashed: relaxed vacancy. The lattice parameter, in abscissa, is measured from the equilibrium lattice parameter at 0 K. All determinants are in units of the exact bulk value at Δa=0. Note the logarithmic scale. Dots correspond to calculated points. Lines are drawn only to help the eye. Both exact values and values obtained from MD trajectories are plotted, but differences are smaller than the dot size (see Ref.24).

T	L_{bulk}	$L_{vac.}$	s_{CL}	s_{CP}	f_{CL}	g_{CP}	v_F
0.01	1.5643	1.5638	0.00	0.00	7.76	7.76	0.97
20.00	1.5677	1.5673	1.35	1.26	7.67	7.67	0.98
40.00	1.5817	1.5818	1.74	1.78	7.41	7.41	1.00
60.00	1.5992	1.5994	1.59	1.69	7.11	7.11	1.01
80.00	1.6164	1.6164	1.27	1.28	6.86	6.86	1.00
0.01	1.5643	1.5638	0.00	0.00	7.76	7.76	0.96
20.00	1.5677	1.5673	1.35	1.25	7.67	7.67	0.98
40.00	1.5817	1.5818	1.74	1.77	7.41	7.41	1.00
60.00	1.5992	1.5994	1.58	1.69	7.12	7.12	1.01
80.00	1.6164	1.6164	1.27	1.30	6.86	6.86	1.00

Table I. Comparison of various thermodynamic properties of the vacancy in argon calculated according to Quasi-harmonic Lattice Dynamics. T is in kelvin degrees, L represents the equilibrium lattice constant at a given temperature in reduced argon units, s_{CL} and s_{CP} are the entropies of formation in units of k_B at constant lattice parameter and constant (zero) pressure, f_{CL} and g_{CP} are the free energy of formation at constant lattice parameter and constant (zero) pressure in reduced argon units, and finally v_F is the volume of formation of the vacancy measured in units of bulk atomic volumes. The upper portion of the table refers to results obtained from exact dynamical matrices; the lower portion to results obtained from dynamical matrices derived from MD trajectyories. The comparison of all quantities is excellent (see Ref.24).

SILICON PHONONS FROM MOLECULAR-DYNAMICS TRAJECTORIES

The method is here applied for the first time to a semiconducting system (the silicon 8-atom supercell) for which benchmark results are available from previous work [20], and proves to be efficient. The dynamical matrix of an 8-atom supercell was calculated for three different volumes. For the electronic part norm-conserving pseudopotentials [3], one Baldereschi point [25] and a plane-wave basis set with energy cutoff at 8 Rydberg were used (the same ingredients as Ref.20). Using random initial positions and zero initial velocities, 12 trajectories of 200 steps were run for each volume. The choice of nonzero initial velocities and linearly independent initial conditions would have reduced significantly the number of trajectories [24]. It is useful to repeat that the number of trajectories needed for larger systems, which are the ultimate motivation for this preliminary test, will not increase with the size of the system, but only with its highest degeneracy, so that the use of trajectories, whose computational effort is comparable to usual phonon techniques for the 8-atom bulk crystal, will become by far convenient as the size of the system is increased and/or its symmetry lowered. The results are presented in Fig.2, where the phonon frequencies of the 8-atom supercell are shown as a function of the cell volume (the experimental volume is 1081 a.u.). The solid lines represent the results of Ref.20, obtained with traditional force-constant techniques and identical ingredients for the electronic structure at 5 volumes, and then fitted to straight lines; the dots represent the phonon frequencies derived from MD trajectories.

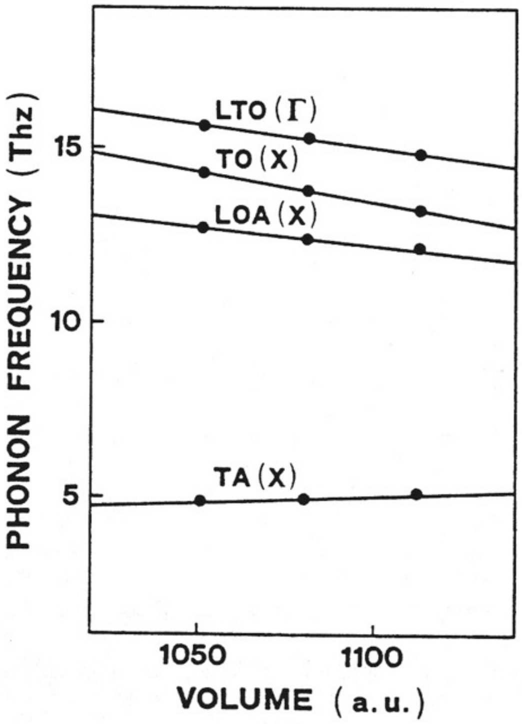

Fig.2 Comparison of phonon frequencies versus volume for an 8-atom silicon crystal. All numbers are derived from first principles calculations based on norm-conserving pseudopotentials and Local Density Approximation; the solid lines result from usual force-constant techniques, while dots are obtained from low-temperature Molecular-Dynamics trajectories (see text).

The good agreement is evident and represents an important test of feasibility of the new method for semiconducting systems. It also confirms that Molecular-Dynamics trajectories generated in the Car-Parrinello scheme are strictly adiabatic and can be regarded from our point of view as real physical trajectories. The test provides the necessary confidence to undertake bulk and vacancy calculations for larger silicon supercells (64 atoms), which are underway [26].

CONCLUSIONS

I have presented a preliminary, successful test of a method recently proposed by Bachelet and De Lorenzi, which extracts dynamical matrices from Molecular Dynamics trajectories. The method, which relies on the possibility of producing Molecular-Dynamics trajectories for semiconducting systems in the Car-Parrinello scheme, is shown to reproduce benchmark results for an 8-atom silicon crystal with periodic boundary conditions. It offers itself as a promising tool to obtain dynamical matrices for semiconductors of large size and low symmetry, and thus (within the quasi-harmonic LD theory) thermodynamic properties of amorphous and defect systems from first principles.

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