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A Dynamical Approach to the α–β Displacive Transition of Quartz

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Abstract

The problem of displacive phase transitions (by which crystals pass on heating from a less symmetric to a more symmetric form) is investigated through numerical integration of the Newton equations of motion for a realistic model, in the paradigmatic case of quartz. Usually such transitions are discussed in terms of the positions of the atoms, while the role of normal modes is emphasized here. The key preliminary property established, in agreement with the indications given by Landau in his thermodynamic-like approach, is that four well definite modes are sufficient to describe the transition, the remaining modes just acting as a noise. The main result is then that such four modes constitute a closed Hamiltonian subsystem presenting an effective potential parametrically dependent on specific energy. The effective potential is actually computed, through (appropriately defined) time-averages of the accelerations of the relevant modes, and is found to describe, as energy is varied, a pitchfork bifurcation, once more confirming in dynamical terms the Landau result. The effective potential also allows one to advance a possible explanation of the "soft mode" phenomenon, namely the occuring, in the Raman spectrum, of a peak whose frequency depends on temperature and vanishes at the transition.

Keywords Phase transition · Molecular dynamics · Crystal structure · Critical exponent

1 Introduction

Already in his celebrated work in which order parameters were introduced (see [1]), Landau discussed displacive phase transitions, indicating them as a possible example of second-order transitions. Displacive transitions are characterized by the fact that, as temperature is increased, crystals pass from a less symmetric structure to a more symmetric one, thus per-

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forming the first step towards melting, where the liquid phase presents a complete rotational symmetry.

In the present paper we study the paradigmatic case of the so-called α-β transition of quartz, using an approach different from the Landau one. Indeed, while he tackled the problem from a thermodynamic point of view, we follow instead a completely dynamical approach, looking for the dynamical element which determines the occurring of the transition. A preliminary key point consists in introducing appropriate order parameters which allow one to describe the transition through a reduced dynamics, involving a small number of degrees of freedom. Now, the order parameters usually considered are defined and discussed in terms of positions of the atoms (see the review [2]). On the other hand Landau pointed out that natural order parameters are the coordinates of the four normal modes of the primitive cell, that have vanishing wave vector $\mathbf{k}$, and are also totally symmetric, in the sense explained in the next section. Then his main result was the construction of a free energy that, as temperature is increased, describes the transition as an (inverse) pitchfork bifurcation.

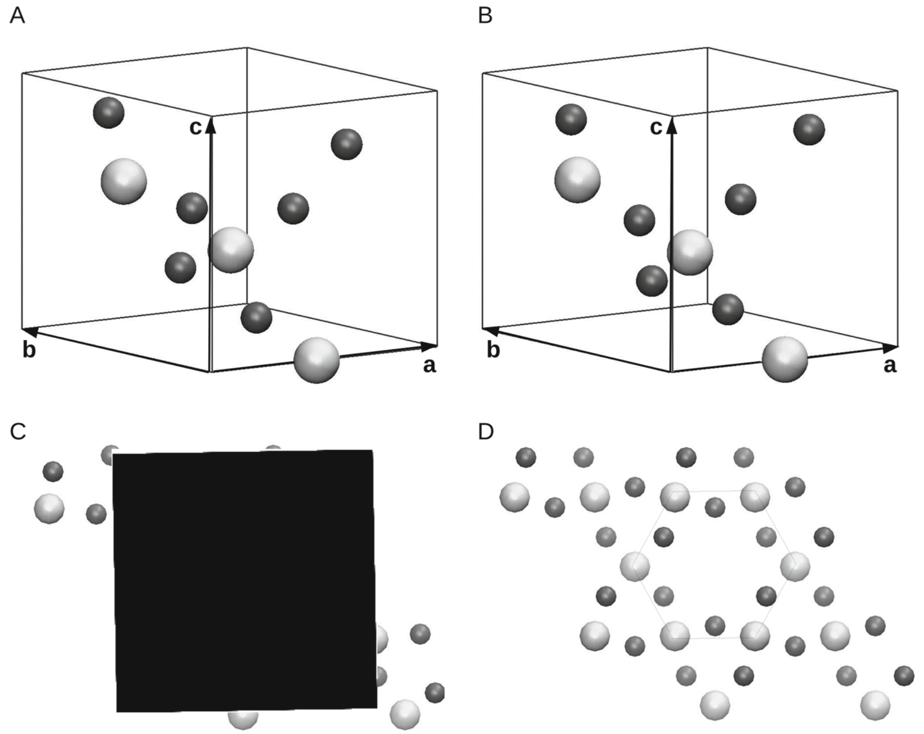
The original contribution of this work consists in showing that, in the particular case of quartz, the classical dynamics of such four relevant modes is well described by a reduced Hamiltonian which presents an effective potential depending parametrically on specific energy. The effective potential is actually calculated. and the transition is shown to occur, as energy is increased, as a pitchfork bifurcation, in analogy with the original thermodynamic-like result of Landau. We finally discuss the soft mode phenomenon, which was unknown in Landau's time and was much discussed later. It consists in the fact that in the Raman spectrum a peak exists whose frequency depends on temperature and vanishes at the transition. This is commonly interpreted as due to the vanishing of the frequency of a "lattice vibration", while we show that, in the case of quartz, what vanishes is a frequency related to the effective potential. The corresponding critical exponent is also calculated.

The paper is organized as follows. In Sect. 2 we recall some details about the structure of the quartz crystal and its symmetries, and explain why the analysis in terms of normal modes is more convenient than in terms of atomic positions. In Sect. 3 are given some details on the atomic model of quartz used in the numerical computations. In Sect. 4 we show how the system breaks down into the relevant sub system of just four modes and a reservoir, while in Sect. 5 we show how the transition is described in terms of the relevant modes. In Sect. 6 the effective potential is constructed, showing how it exhibits a pitchfork bifurcation. The existence of a soft mode is discussed in Sect. 7. The conclusions follow.

2 Symmetries, Structures and Order Parameters of Quartz

In this Section we will introduce the order parameters which are suited for describing the transition from α–quartz to β–quartz, explaining in particular why they are just four, as illustrated for example in the work [3]. To this end it is necessary to recall some details about the structure of quartz. The primitive cell of the crystal lattice (Fig. 1), which contains six Oxygens and three Silicons, has the form of a right prism with a rhomboidal base, defined by basis vectors $\mathbf{a}$ and $\mathbf{b}$ of equal length forming an angle of $2\pi/3$, and $\mathbf{c}$, orthogonal to the plane of $\mathbf{a}$ and $\mathbf{b}$. The lengths of such vectors depend in general on temperature and pressure, but in our simulations they are kept fixed since, for reasons of simplicity, we chose to work at constant volume.

What distinguishes the α and the β phases is the arrangement of the atoms within the cell and the different number of discrete symmetries they possess. Indeed the α structure



[redacted]

Fig. 1 The quartz cell. Atoms are represented as spheres (smaller and darker for Oxygen, larger and lighter for Silicon). Upper row: primitive cell of the quartz crystal, α phase left (**A**), β phase right (**B**). Lower row: projection of four adjacent cells on the **a b** plane in the α phase left (**C**), and in the β phase right (**D**). Selected Silicon atoms are shown to lie on the vertices of an irregular hexagon in the α phase, while in the β phase they form a regular hexagon

is invariant under a group of six transformations that constitute a subgroup of the twelve symmetries of the β structure. Such symmetries are recalled here in a footnote[1]

This is illustrated in the lower panels of Fig. 1, in which four adjacent cells are projected on the **ab** plane: in the α phase (left), six Silicon atoms lie on the vertices of an irregular hexagon, which is symmetric under rotations by $2\pi/3$, while in the β phase (right) the same atoms form a regular hexagon with symmetry under $\pi/3$ rotations.

Now, evidently such symmetries constrain the possible microscopic configurations of the atoms of the cell. It turns out that the configurations with α symmetry are labeled by four independent parameters, while those with β symmetry are labeled by just one parameter. In geometric terms, the structures with α symmetry form a four-dimensional sub manifold in configuration space, while those with β symmetry lie on a curve belonging to that sub manifold, since every β configuration possesses α symmetry as well.

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[1] Quartz may be left-handed or right-handed, and here we concentrate on the left-handed one. The symmetry group of left-handed α-quartz, $P3_221$, is generated by two transformations: a rotation by π around axis **a**, and a rototranslation made up of a rotation by $2\pi/3$ around axis **c**, followed by a translation by $2\mathbf{c}/3$ ($\mathbf{c}/3$ for the right-handed symmetry group, $P3_121$). The symmetry group of left-handed β-quartz, $P6_222$, is generated by the same rotation by π around axis **a**, whereas the rototranslation consists of a rotation around **c** by $\pi/3$ followed by a translation by $\mathbf{c}/3$ ($2\mathbf{c}/3$ for the right-handed group $P6_422$).

Let us now come to the problem of parameterizing such a four-dimensional manifold, i.e., of choosing suitable coordinates. In the literature every atomic position $\mathbf{r}$ in the primitive cell is expressed by means of "fractional coordinates", as $\mathbf{r} = x\mathbf{a} + y\mathbf{b} + z\mathbf{c}$. The α structure may then be defined in terms of such coordinates in the following way: having arbitrarily fixed the position of one Oxygen atom in the cell, consider its orbit under the transformations of the group (i.e., the points obtained by applying the six transformations of the symmetry group): the orbit will consist of six (generally distinct) points, which will permute among themselves upon a group transformation. Accordingly, the orbit of the point determines an invariant configuration of the Oxygen atoms. Since the Silicon atoms are only three, they have to correspond to orbits consisting of just three points: thus the initial point is constrained to lie on the $\mathbf{a}$-axis.[2] Therefore, the four parameters can be chosen as the three fractional coordinates x_O, y_O, and z_O of an Oxygen atom, and the coordinate x_S of a Silicon atom. As for β quartz, its symmetry group has twelve elements, so that the position of the Oxygen atom is constrained as well: only positions whose orbit is made up of just six distinct points have to be taken into account: this implies $x_O = 2y_O$ and $z_O = 1/6$. For the position of the Silicon atom, the requirement of an orbit made up of three distinct points gives the further constraint $x_S = 1/2$. All that proves that β configurations are parameterized by a single parameter (x_O, for example).

Thus, as an order parameter one can choose either the four mentioned fractional coordinates, or the single one defined by:

$$\eta = \frac{\sqrt{(2x_S - 1)^2 + (2y_O/x_O - 1)^2 + (6z_O - 1)^2}}{\eta_0}\ , \tag{1}$$

(with a normalization constant η_0 to be specified later) which entails, on vanishing, that the transition to the β phase is accomplished.

Now we set forth a different choice, based on the normal-mode coordinates, which turns out to be much more convenient.

Having chosen a Hamiltonian suited for describing quartz, with its known symmetries, the potential will have two absolute minima (symmetric with respect to rotations by π around $\mathbf{c}$) and in the α phase, since the α-quartz is the thermodynamically stable phase of quartz at low temperatures. Let's single out one of such equilibrium points. Normal modes $A^{(j)}_{\mathbf{k}}$ can be introduced, which are parameterized by the wave vector $\mathbf{k}$ and by an index $j = 1, \ldots, 27$, labeling the solutions of the secular equation ($27 = 3 \cdot 9$ being the coordinates of the atoms in a cell). The configuration with all $A^{(j)}_{\mathbf{k}}$ vanishing corresponds to the considered minimum. Other crystal configurations are obtained by varying the coordinates $A^{(j)}_{\mathbf{k}}$ with $\mathbf{k} = 0$, while keeping all other coordinates to zero (to preserve the same periodicity). However, in order to keep the α symmetry, the only normal modes that may be excited are the totally symmetric ones, i.e., those invariant under all transformations of the symmetry group. It is not surprising that there are only four normal modes with this property, exactly as the number of fractional coordinates needed to describe the α structure.[3]

The coordinates of such normal modes, henceforth denoted by A_1, A_2, A_3, and A_4, are precisely the order parameters we intend to use. In fact, it is apparent that, since the β configurations are a subset of the possible α configurations, they will be obtained by exciting the totally symmetric normal modes only. Moreover, it can be shown that they must satisfy

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[2] In this case, indeed, the action of the first group generator, i.e. the rotation by π around axis $\mathbf{a}$, coincides with the identity and, consequently, the orbit consists of three points instead of six.

[3] These modes are not active in the infrared spectrum, but can be detected for example in the Raman spectrum.

the relation

$$(A_1, \ldots, A_4) = \mathbf{A}^0 + \lambda \mathbf{A}^\beta \ , \tag{2}$$

where λ is a free parameter, $\mathbf{A}^0$ represents the average of the two minimum–energy α structures (which has β symmetry) and

$$\mathbf{A}^\beta = (0.08348, -0.98198, 0.16040, -0.05492)$$

is the unit vector describing the linear one-dimensional sub manifold of all configurations with β symmetry.

Thus the advantage of using normal modes becomes evident: the configuration of the cell is defined by only four well definite mode coordinates, and these are the only ones that are expected to oscillate about non vanishing values. The huge number of the remaining modes are instead expected to have coordinates that keep oscillating about the zero value. So one meets here with a dynamical decomposition into two subsystems (the relevant one and the reservoir). This is a property, illustrated in Fig. 2, which underlies the whole present paper.

3 The Model

Some details are now given concerning the molecular dynamics simulations performed in this work. Quartz and other crystals exhibiting displacive phase transitions have been the subject of many molecular dynamics studies, beginning with the early works by Tsuneyuki et al. [4, 5], and several force fields were developed [6] and applied to the study of such phenomena (see e.g. [7] for a comparison of different force fields in the study of phase transitions). In all such papers, only atomic positions (rather than normal modes) were investigated.

Coming to our work, since it is intended as having a prevalently qualitative character, the computations were performed in the spirit of ergodic theory, i.e., without making any attempt at simulating realistic situations involving fixed pressure. So we worked at fixed volume, setting the lengths of the basis vectors of the cell at their experimental values [8] at standard conditions. Analogously, in place of temperature we chose as a parameter specific energy ε, i.e., the total energy per degree of freedom (expressed in kelvin, after dividing it by the Boltzmann constant).

So we use a model consisting of N massive points located in a "working box" of volume V, consisting of $k \times k \times k$ (k a positive integer) primitive cells with periodic boundary conditions. Since, as already recalled, each cell is constituted by three SiO_2 groups, the whole working box contains $N = 9k^3$ atoms.

The corresponding Hamiltonian is then given by

$$H = \sum \frac{\mathbf{p}_i^2}{2m_j} + \sum_{i \neq j} V_{ij}(r_{ij}) \ ,$$

where $\mathbf{x}_i$, $\mathbf{p}_i$ are the canonical coordinates of the i–th atom, m_i the corresponding mass ($m = 16$ a.m.u. for the Oxygen atoms, $m = 28$ a.m.u. for the Silicon ones), V_{ij} is the interaction potential between the i-th and the j-th atom while $r_{ij} = |\mathbf{x}_i - \mathbf{x}_j|$ is their distance. For what concerns the microscopic inter atomic potentials V_{ij}, whose choice is indeed a delicate point, we just employed the well known BKS one [9]:

$$V_{ij}(r) = \frac{e_i e_j}{r} + A_{ij} e^{-B_{ij} r} - \frac{C_{ij}}{r^6} \ ,$$

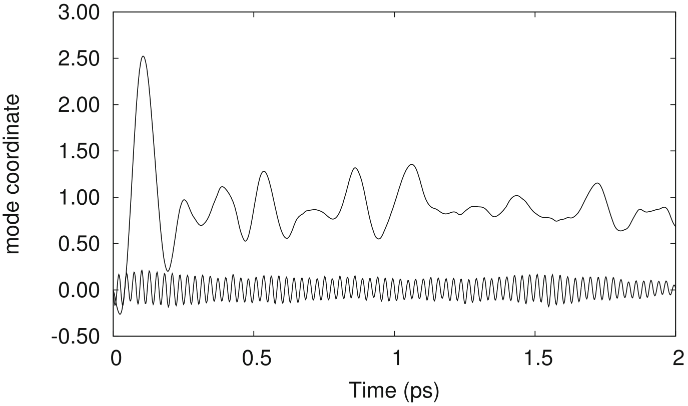

Fig. 2 Relevant and not relevant mode. Starting from a vanishing value of all mode coordinates, with a Maxwell–Boltzmann distributed kinetic energy, a few modes modes jump to a finite mean value, then oscillating about it, and are relevant for the configuration of the crystal, while the remaining ones keep oscillating about the initial vanishing value, producing noise. An example of the first kind and one of the second are shown, at a specific energy of 300 K

where e_i and e_j are the "effective charges" of the atoms ($2.4\,e$ for Silicon and $-1.2\,e$ for Oxygen), and the parameters A_{ij}, B_{ij}, C_{ij} for O–O, Si–Si and O–Si pairs are given in ref. [9]. A cutoff of 9 Å is imposed on the short–range part of the potential,[4] while for the Coulomb long range forces the standard Ewald summation rule (see for example papers [10, 11]) is used.

Being the model Hamiltonian, its integration is performed through the standard symplectic Verlet (or leap–frog) algorithm with a time step of typically 2 femtoseconds. All simulations are performed at fixed volume, actually the one determined by the given lattice vectors. Notice that, since the atoms are dealt with as point like, we cannot reproduce the Raman effect, which requires, as is well known, a deformable atomic model. However, it will be later shown how the chosen model allows one to exhibit a characteristic feature denoted "the soft mode", i.e., the existence of a frequency that depends on temperature and vanishes at the transition.

We checked that, with the chosen potential, there are indeed two points of absolute minimum corresponding to an α structure: one with fractional coordinates (0.46478, 0, 0) and (0.42683, 0.27152, 0.12488) for the Silicon and for the Oxygen reference atom respectively; and the other one with fractional coordinates (0.53521, 0, 0) and (0.42683, 0.15531, 0.20846) respectively. We also checked that the potential has a local maximum corresponding to a β structure with fractional coordinates (0.42373, 0.21186, 0.16667) for Oxygen and (0.5, 0, 0) for Silicon.

The initial data were assigned by setting the system in one of the two minima of the potential energy and generating random velocities of the particles, according to a Maxwell–Boltzmann distribution.

For each value of the energy, 20 different orbits (each with a time–length of 400 picoseconds) were computed, 10 starting in one minimum, and 10 starting in the other one. The averages were always meant as time averages along each orbit (in some cases restricted to the last 200 ps), followed by a further average over the 20 different orbits.

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[4] Due to the presence of the cutoff, one needs to take a working box made at least of 2 × 2 × 2 primitive cells.

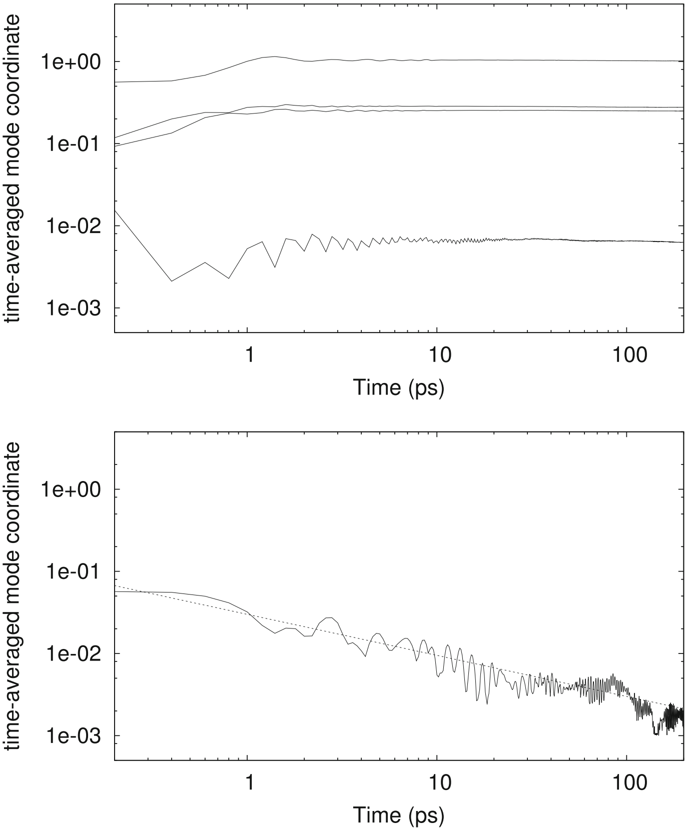

Fig. 3 The dynamical decomposition. Time averages of mode coordinates vs. time, in log–log scale at 300 K. Upper panel: the four relevant modes. Lower panel: the maximum of the absolute values of all the remaining modes. Compare with the dashed line with slope -1/2 (see text)

4 The Decomposition into a Relevant Subsystem and a Reservoir

The mentioned dynamical decomposition of our model of quartz into the two subsystems of the relevant and the non relevant modes is vividly exhibited by numerical simulations. Having chosen initial data with vanishing values of the coordinates of all modes, and with a certain kinetic energy (corresponding to a specific energy of 300 K, in the present case), the subsequent evolution of the system is illustrated in Fig. 2, which refers to a number of particles $N = 576$, i.e., a working box of $4 \times 4 \times 4$ primitive cells. In the figure are reported, versus time, the instantaneous coordinates of two chosen modes, and it is seen that one of them keeps oscillating about the initial vanishing value. Instead the other one performs an initial jump and then oscillates (rather irregularly) about a non vanishing value.

Figure 3 illustrates how there are just four modes which are excited, the ones which are relevant for the α configuration. In the upper panel are indeed reported time-averaged coordinates of such modes (in absolute value) rather than instantaneous values (still versus time, but in log-log scale), and they are seen to stabilize at certain non vanishing values, after a transient of the order of ten picoseconds.

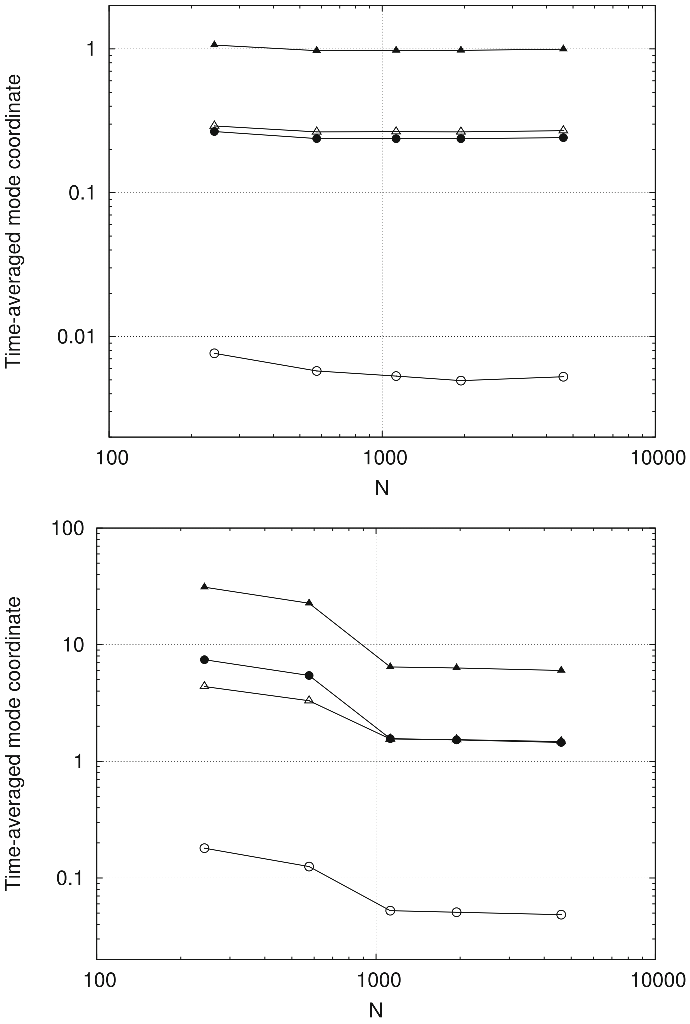

Fig. 4 Dependence of the results on the number N of atoms. The value of the time-averaged coordinate of the four relevant modes as a function of the number N of particles, from $N = 243$ to $N = 4608$, at two specific energies: $\varepsilon = 300$ K (upper panel), and $\varepsilon = 1250$ K (lower panel)

In the lower panel of Fig. 3, instead, we report the maximum, among the remaining modes, of the (absolute value of the) time averages of the mode coordinates. Such a single collective curve is sufficient to show that all their time-averaged coordinates keep diminishing, apparently towards a vanishing value. The maximum is seen to decrease as the inverse square root of the time over which the average is performed (dotted line), as should be expected if, in the $t \to \infty$ limit, the time averages actually vanished. Thus the motions of the coordinates of the non relevant modes just consist of fluctuations about the zero value.

So, dynamically the system is seen to actually be decomposed into two subsystems: the first one, composed of the four *relevant modes*, and the other one constituted by all remaining modes, that might be called *the reservoir*, since it just acts on the relevant one as a dynamical noise. Such a phenomenon, first observed at specific energy $\varepsilon = 300$ K, was found to occur for all specific energies investigated in our simulations, from 300 K up to 3000 K. This was in fact for us a kind of "little discovery", that actually happened to give origin to the present research.[5]

In the case of $\varepsilon = 300$ K it also occurs that the values themselves of the time-averaged mode coordinates are even essentially equal for N ranging from $N = 243$ to $N = 4608$, as shown in the upper panel of Fig. 4. This can be described by saying that the asymptotic value is already attained with a model of 576 atoms (admitting that one is actually dealing with the asymptotic value, i.e., that other changes would not be found at further larger values of N). Instead, in the case of $\varepsilon = 1250$ K (lower panel of the same Fig. 4) the situation may be described by saying that the asymptotic value is attained with 1125 atoms (and then kept for larger values). We have indications that the number of atoms required for attaining the asymptotic value increases with the specific energy. However a search for such a number N of atoms as a function of ε is beyond the aims of the present paper. Our central aim is indeed to exhibit that a dynamical implementation of the result obtained by Landau through thermodynamic-like methods is altogether possible. Thus, in the present research we chose to work altogether with $N = 576$ atoms, deferring a determination of the optimal N as a function of ε to a future work. Indeed we are confident that we will also have available an analytical formula of the effective potential, obtained through suitable large deviations methods, so that a determination of an optimal minimal value of atoms in the numerical model will be really possible.

5 The Transition in Terms of the Relevant Modes

As specific energy is increased above 300 K, it is found that the time-averaged coordinates of the four relevant modes increase (in modulus), with the system still remaining in the α structure. Instead, if energy is sufficiently raised, the system exhibits a transition to the β phase.

The transition is neatly exhibited by means of the order parameter η defined by relation 1 in Sect. 2, with the normalization constant given by

$$\eta_0 = \sqrt{(2x_S^\alpha - 1)^2 + (2y_O^\alpha/x_O^\alpha - 1)^2 + (6z_O^\alpha - 1)^2}\ ,$$

where x_S^α and $(x_O^\alpha, y_O^\alpha, z_O^\alpha)$ are the fractional coordinates in the equilibrium configuration.[6] Such a choice is so made that η vanishes in the β phase (analogously to what occurs for the ferromagnetic transition in terms of magnetization), while being equal to 1 in the extreme α phase, i.e., in the two minima of the potential energy.

From the upper panel of Fig. 5, which reports the order parameter η versus specific energy, the transition is seen to occur at a specific energy of about 1500 K.

It is worth noting that the fractional coordinates of the β phase depend very little on specific energy, since x_O ranges from 0.432 at $\varepsilon = 1500$ K to 0.433 at $\varepsilon = 1900$ K. In any case such values are definitely different from the fractional coordinate x_O pertaining to the local maximum of the mechanical potential, which is $x_O \simeq 0.424$.

However the transition may as well be displayed directly in terms of the coordinates of the relevant modes. In fact in the lower panel of the same Fig. 5 are shown, still versus specific

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[5] This occurred when studying the infrared spectrum of quartz (see [12]).

[6] We recall that there are two equilibrium points, but, by symmetry, the value of the normalizing constant η_0, turns out to be the same.

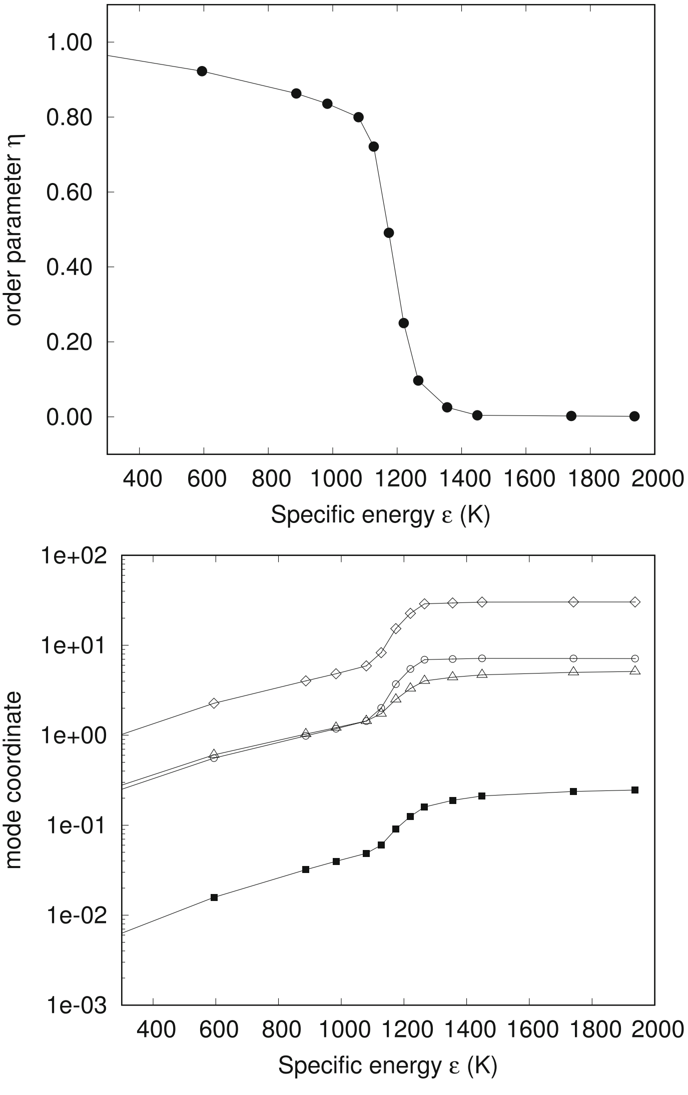

Fig. 5 Evidence for the α–β transition. Upper panel: order parameter η vs. specific energy. Lower panel: coordinates of the four relevant modes vs. specific energy (in semi logarithmic scale)

energy, the time averages of the coordinates (in absolute value) of the four relevant modes.[7] This figure exhibits, for all such modes, a behavior correlated to that of the order parameter. Indeed, after a moderate increase at lower energies, such averaged coordinates present an abrupt change of slope at about 1100 K, and then become almost constant starting from about 1500 K. This corresponds to the value of specific energy at which the $\alpha - \beta$ phase transition macroscopically occurs, since it can be checked that relation (2) of Sect. 2 holds.

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[7] Recall the time averages are further averaged on a sample of 20 orbits, half of which start in one minimum of the potential, and the remaining orbits in the other one. The normal modes are computed with reference to the minimum from which the orbit starts.

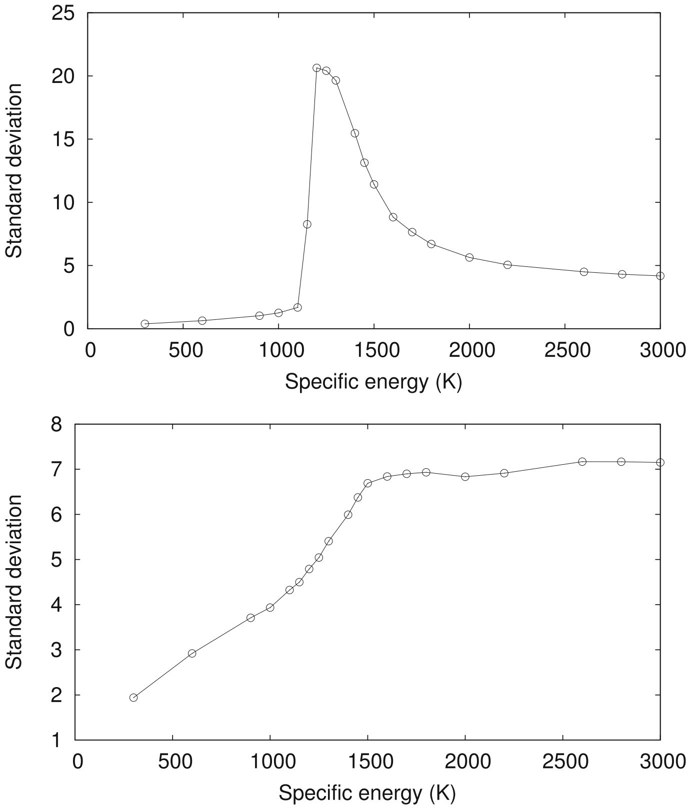

Fig. 6 Fluctuations of normal mode coordinates vs. specific energy. Upper panel: standard deviation of the relevant-mode coordinate A_1. The peak is in correspondence with the phase transition. Lower panel: maximum of the standard deviations of the coordinates of all non relevant modes

Particularly relevant is the fact that, at the transition, the coordinates of the two "highest" modes appear to have attained values which remain constant for larger specific energies, which is a signature of a non-analytic behavior characterizing the occurring of a phase transition. Moreover, this turns out to occur already for a finite number N of atoms, without any need of approaching the thermodynamic limit. However, the details of the transition appear to have some dependence on N: indeed the data shown in the lower panel of Fig. 4 indicate that at $\varepsilon = 1250$ K the system is still completely in the α phase for $N > 576$, while it is already passing to the β phase for $N = 243$ and for $N = 576$. This suggests that the critical specific energy varies with N, but, as already stated, a systematic determination of this dependence is beyond the scope of the present work.

A different way to see that a transition occurs, is to look at the standard deviation of the mode coordinates, rather than at their averages. In Fig. 6, upper panel, we report the standard deviation σ_{A_1} versus specific energy. Such a standard deviation is seen to present a very evident peak at the transition. This is in qualitative agreement with what is in general maintained, i.e., that fluctuations should "diverge" (in the thermodynamic limit) at a phase transition. The reason of such a behavior will be illustrated in the next Section, in connection with a flatness property of the effective potential.

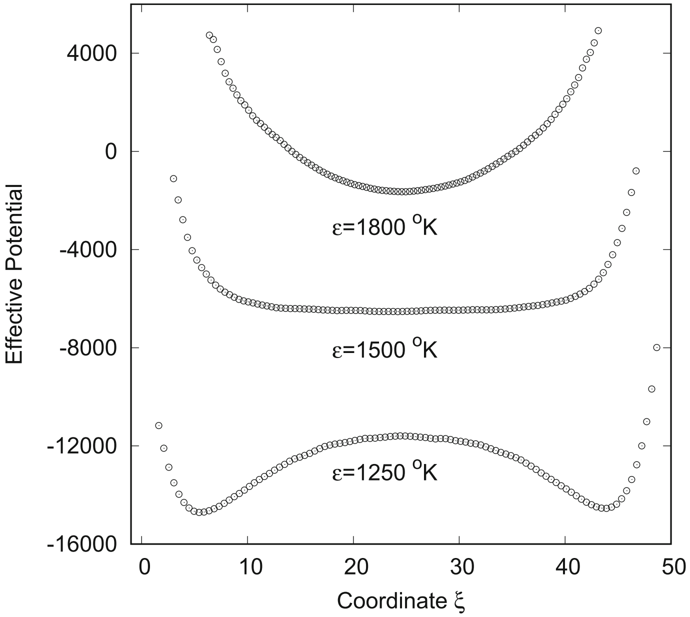

Fig. 7 The calculated effective potential. Plot along the segment (coordinate ξ) joining the two minima of the inter atomic potential, for three values of specific energy. Notice that, for the sake of illustration, a constant term (depending on specific energy) was added

In the lower panel of the same Fig. 6, we report the maximum of the variances of the coordinates of the modes of the reservoir (i.e., all modes different from the four relevant ones). As one sees, such variances show no signature of a possible divergence at the transition, but rather seem to present a smooth approach to a plateau above the transition. This is another indication that only the four relevant modes are involved in the transition.

6 The Energy-Dependent Effective Potential

The results illustrated in Sect. 4 about the decomposition of the global system into the subsystem of the relevant modes and a reservoir, suggest that a reduced dynamics may exist for the subsystem of relevant modes with coordinates $\mathbf{A} = (A_1, A_2, A_3, A_4)$, being governed by an energy-dependent effective potential $V_{\text{eff}}(\mathbf{A}, \varepsilon)$. Work is in progress for obtaining an analytical formula for such an effective potential, using large deviations methods. Here we just limit ourselves to assume that the potential exists, and show how it is actually computed numerically through time averages.

The effective potential is computed along the direction that, in the space $\mathbf{A} = (A_1, A_2, A_3, A_4)$ of the relevant modes, joins the two points of minimum of the microscopic potential. Denoting by ξ the coordinate along such an axis, i.e., the scalar product $\xi = \mathbf{A} \cdot \mathbf{e}$ where $\mathbf{e} = (0.9669, -0.2375, -0.0927, 0.0019)$ is the unit vector defining such a direction, the computation is performed in terms of time averages in the following way.[8] Given a value of ξ attained along a given orbit at a certain time, one can compute by ele-

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[8] Such a method is analogous to the one we already used for computing the effective potential acting among the two protons in the ion of the Hydrogen molecule—see [13]. Interestingly enough, in that case the potential,

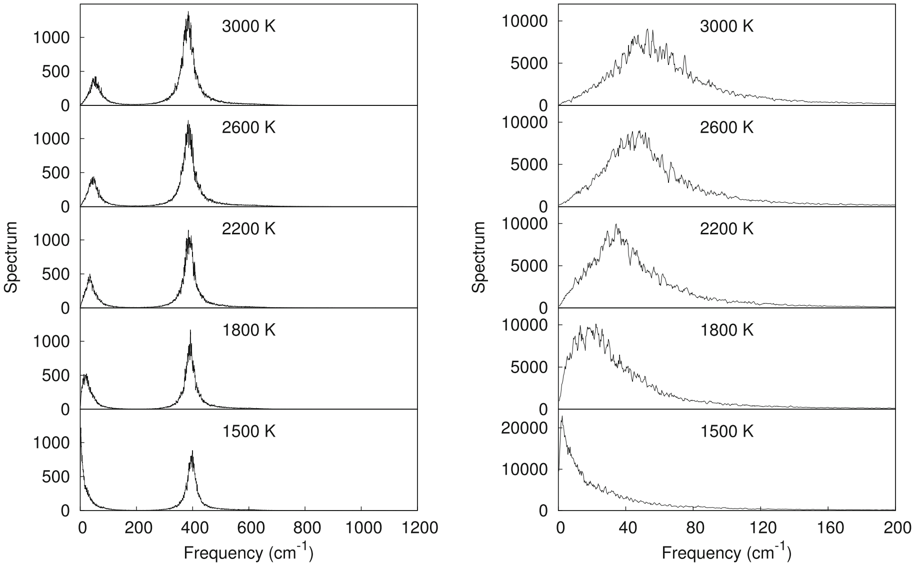

Fig. 8 The soft mode phenomenon. Spectrum (.i.e. the Fourier transform of position-velocity time correlation) of the mode A_3 (left) and that of the coordinate ξ (right) for several specific energies. Notice the peak which moves towards a vanishing frequency, as the specific energy attains the critical one

mentary formulas the corresponding acceleration $\ddot{\xi}$. Thus, by collecting all such pairs from all simulations at a given specific energy, irrespectively of where the orbit is coming from, a large sample of $(\xi, \ddot{\xi})$ pairs is obtained. The mean acceleration $\ddot{\xi}$ as a function of ξ is then determined by dividing the range spanned by the collected values of ξ into a certain number (100) of bins and calculating the average values of $\ddot{\xi}$ over all points with ξ in each bin.[9] By further integrating with respect to ξ, the effective potential is then easily calculated (apart from an additive constant).

The results are shown in Fig. 7, for three values of specific energy, i.e., $\varepsilon = 1250$ K, 1500 K and 1800 K. The figure clearly shows that the effective potential exhibits a pitchfork bifurcation when the system passes from the high-energy phase to the low-energy one. Moreover, the potential is seen to be extremely flat at the transition. This fact explains the peak of the variance of the coordinate A_1 at the transition (Fig. 6, upper panel), since at the transition such a coordinate is free to have conspicuous departures from the equilibrium position. Such a fact also corresponds to the occurrence of a soft mode, as we will see in the next Section.

7 The Soft Mode Phenomenon and Its Critical Exponent

The Raman spectrum of quartz presents a remarkable peculiarity. Namely, among its several peaks there is one whose position strongly depends on temperature; moreover, the frequency ω_0 corresponding to the maximum of that peak vanishes at the transition. This is the phe-

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still defined through time averages, turned out to exist only in the presence of ordered, rather than chaotic, motions. On the other hand, ordered motions are met also in the present case, just in virtue of the definition itself of a displacive transition.

[9] So we are actually performing a time average, restricted to suitably defined discrete times.

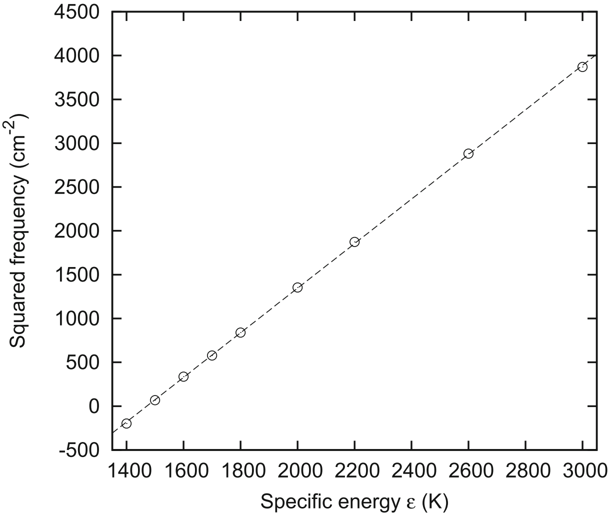

Fig. 9 Critical exponent for the soft mode. Squared characteristic frequency associated to the effective potential near the transition and above it vs. specific energy. Dotted line is a linear regression interpolation

nomenon known in the literature as “soft mode”. The name refers to the current interpretation, according to which there exists a normal mode of the system (called a “lattice vibration” in reference [2]) whose frequency is the one vanishing at the transition.

In our case such a phenomenon cannot be investigated in a direct way since, as explained in Sect. 2, our model deals with rigid atoms, so that the Raman spectrum vanishes. It is nevertheless possible to test the idea that a normal mode with a frequency vanishing at the transition actually exists in our model. The key point is first of all that, at variance with what is done in the literature, we do not consider normal modes of the β configuration, for the simple reason that such a β configuration is not an equilibrium configuration, so that it doesn’t involve normal modes at all.

Things change however if one considers the four modes A_j relevant for the transition which, as mentioned in Sect. 2 are known to be active for the Raman effect. In Fig. 8, we report, on the left, the spectrum, for example, of A_3, i.e., the Fourier transform of the time correlation between A_3 and $\dot{A}_3$, at different specific energies. As one can see, there are two peaks centered at different frequencies, one of which vanishes at the transition. Instead, if one looks at the spectrum of the variable ξ (same figure on the right), for energies above the transition it shows just one peak, essentially the one which appears also in the spectrum of A_3 at the lower frequencies. So the phenomenon of the soft mode should not be due to a single normal mode, but to the variable ξ, namely, the linear combination of the coordinates of the relevant normal modes that determines the phase transition.

The relevant peak in the spectrum of ξ can be easily understood in terms of the effective potential. Indeed its shape at high energies naturally suggests the existence of a characteristic frequency ω_0 in the spectrum of the variable ξ, namely, the frequency of the small oscillations about the minimum of the effective potential. In order to calculate this quantity, at each value of specific energy ε the curve of the acceleration $\ddot{\xi}$ as a function of ξ was analyzed in the region $15 < \xi < 35$, where it turns out to be linear, and its slope, computed by linear regression, was identified with $-\omega_0^2(\varepsilon)$. The results are reported in Fig. 9 for specific energies in the interval [1400, 3000] K. Such a figure is the analogue of Fig. 9 of the review [3], taken from

[14], obtained by inelastic neutron scattering. As is clearly shown by the superimposed linear interpolation (dotted line), $\omega_0^2(\varepsilon)$ has a linear dependence on specific energy ε, and vanishes at $\varepsilon = \varepsilon_{cr} \simeq 1471$ K. The latter value can be interpreted as an estimate of the critical specific energy in our model, i.e., the specific energy at which the $\alpha - \beta$ transition occurs: indeed, the bifurcation of the effective potential can take place only if at the minimum the second derivative vanishes. The characteristic frequency associated to ξ is thus seen to pass through the zero value when the transition energy is attained from above. Notice also that the linear dependence of $\omega_0^2(\varepsilon)$ on specific energy implies a relationship $\omega_0(\varepsilon) \sim \sqrt{\varepsilon - \varepsilon_{cr}}$, so that the critical exponent has value 1/2. As in this range of energies temperature should be proportional to specific energy ε (apart from an additive constant), this result is apparently in agreement with the experimental data.[10]

In conclusion, we are suggesting that the phenomenon of the "soft mode" is due to the same mechanism, the bifurcation of the effective potential, that determines the phase transition.

8 Conclusion and Perspectives

The central aim of the present work was to exhibit that the problem of displacive phase transitions can be addressed in (classical) dynamical terms, thus complementing the Landau thermodynamic-like approach. A first step was implemented here.

Indeed the main Landau result, i.e., that the transition is completely described in terms of a suitable free energy depending only on four macroscopic variables and temperature, is here recovered in dynamical terms. In fact, such four variables are just the normal mode coordinates already indicated by Landau, and the place of the thermodynamic free energy is taken by an effective purely mechanical potential dependent on specific energy. Such a potential enters the effective Hamiltonian that is found to govern the motions of the relevant modes, on which the remaining ones just act as a noise. The relation between the thermodynamic free energy and the mechanical effective potential is still unknown to us. Perhaps a difficulty is that we work at a purely mechanical level, with specific energy taking the place of temperature.

It was also shown that a method exists for estimating numerically the effective potential, and a concrete implementation was performed using a quartz model with a small number of atoms. A systematic study of the dependence of the result on the number of atoms was not performed here, and is left for future studies.

We are confident however that such a numerical problem may be soon overcome at all, by making available an analytical formula for the effective potential. Work is in progress, based on suitable large deviations methods.

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Data Availability The data sets generated and analyses during the current study are available from the corresponding author on reasonable request.

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[10] In general, vibrational frequencies vary with volume, and volume changes should be taken into account for a correct estimate of the frequency in question. However, for temperatures above the transition, quartz exhibits negligible thermal expansion [8], so that our fixed-volume computations should be appropriate. On the contrary, below the transition there is a significant change in volume, and the behavior of the soft-mode frequency and of the corresponding critical exponent cannot be estimated in our model.

Declarations

Conflict of interest The authors have no conflict of interest to declare that are relevant to the content of this article.

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