Simulation of Material Properties Below the Debye Temperature: A Path-Integral Molecular Dynamics Case Study of Quartz

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Classical and path integral molecular dynamics (PIMD) simulations are used to study α and β quartz in a large range of temperatures at zero external stress. PIMD account for quantum fluctuations of atomic vibrations, which can modify material properties at temperatures below the Debye temperature. The difference between classical and quantum mechanical results for bond lengths, bond angles, elastic modulii, and some dynamical properties is calculated and comparison to experimental data is done. Only quantum mechanical simulations are able to reflect the correct thermomechanical properties below room temperature. It is discussed in how far classical and PIMD simulations can be helpful in constructing improved potential energy surfaces for silica.

I. INTRODUCTION

Quartz is one of the most abundant and best studied minerals on Earth; the structure and many other physical properties are well understood. Classical molecular dynamics (MD) simulations have been particularly successful in connecting atomic interactions between silicon and oxygen atoms in the condensed phase with structural and elastic properties of quartz and other silica polymorphs at finite temperatures. At zero temperature, this connection has also been done by mere first-principle studies or ab-initio methods incorporating bulk-system informations.

Some of the numerical approaches reach a nearly perfect agreement with experiment, especially for structural properties. None of the calculations, however, include quantum effects of the ionic motion. Quantum effects lead to an equilibrium structure that is different from the “classical” equilibrium structure as soon as the anharmonic interactions must be reflected accurately by the model potential. Overall, ab-initio calculations, MD simulations, and experimental data have partially achieved such good agreement that estimating quantum effects will play an important role in determining the real merits of a potential energy surface.

In this study, path-integral molecular dynamics (PIMD) are used to determine the quantum effects on physical properties of quartz. Due to the large computational demand of path integral simulations, we confine ourselves to the use of only one potential energy surface, namely the BKS potential. It has been particularly successful in reproducing silica properties not only of α-quartz but also of other silica polymorphs and of the glassy state. It is therefore rather plausible that the BKS potential predicts accurately the shifts from classical results to quantum mechanical results.

Recently, β-quartz and β-cristobalite have been investigated by means of path integral Monte Carlo (PIMC) simulations. The PIMC study, however, was only done for phases that are stable at temperatures above 800 K. Quantum effects are relatively small at such high temperatures. Moreover, the resolution of our PIMD simulations exceeds that of the employed PIMC algorithm by orders of magnitudes. E.g., the PIMD approach makes it possible to calculate the ground-state equilibrium lattice constants with a resolution of more than 0.001 Å for a given potential energy surface, while the PIMC simulations had an uncertainty of typically 0.1 Å. This improvement in resolution is possible despite a strong reduction in CPU time. Furthermore, arbitrary parallelepiped simulation cells are permitted in this PIMD study allowing to calculate all elastic constants. The PIMC studies were confined to orthorhombic geometries and did not allow calculations of any elastic constants due to large statistical error bars.

The remainder of this paper is organized as follows: In
Sec. II, the PIMD method used in this study is described along with some specific, technical details. In Sec. III results are presented for structural data, elastic constants, and dynamic properties. Quantum mechanical results are compared to classical simulations and experiment. Conclusions are drawn in Sec. IV.

II. METHOD

A. Path Integral Molecular Dynamics in the Constant Stress Ensemble

Although path integral Monte Carlo (PIMC) is usually used to estimate quantum effects in solids, path integral molecular dynamics (PIMD) arise as a more natural choice for long-range Coulomb interactions. The Ewald sum needed to be evaluated only once per time step in PIMD as opposed to each single local move in PIMC. Moreover, global moves in which the shape and size of the simulation cell are varied, are at basically no extra cost trials move of the strain tensor.

In the path integral formulation of quantum statistical mechanics, a quantum point particle at temperature $PT$ is represented by a closed polymer at temperature $PT$, in which adjacent beads interact via harmonic springs. The stiffness of the springs increases with decreasing thermal de Broglie wavelength $\lambda$ that a free particle would have at temperature $PT$. Studying this model in a molecular dynamics simulation, would require small time steps in the quantum limit $P \rightarrow \infty$, if the dynamical masses of the polymer beads were chosen to be identical with the physical mass $m$ of the quantum particle. However, it is possible to adjust all intra-molecular vibrations to similar time scales if the equations of motion are expressed in a convenient representation and appropriate “dynamical” masses are attributed to the beads. In this study, the coordinates are represented in terms of eigenmodes of the free particle. The dynamical masses $m_\omega$ attributed to the motion of the eigenmode $\omega$ are usually chosen according to $m_\omega = k_E/(k_E + k_\omega)$, with $k_E$ the coupling of an atom to its lattice site in the Einstein model of solids and $k_\omega$ the spring constant associated with eigenmode $\omega$. This choice of dynamical masses allows for efficient sampling of all degrees of freedom, because all modes move essentially on the same time scale. The dynamical mass of the center-of-mass motion of the polymer $\bar{m}_0$ is of course identical with the real mass $m$.

The motion of the simulation cell is constrained to symmetric strain tensors, but otherwise done as is in the classical Parrinello-Rahman method. The dynamical mass $W$ associated with the motion of the simulation cell geometry is again chosen such that a typical oscillation time of the box is close to a typical oscillation time of a silicon or oxygen atom. The choice of $W$ merely controls the efficiency of the sampling but leaves meaningful observables unaffected.

One advantage of the Parrinello-Rahman method is the possibility to determine all elastic constants at zero external stress. This is done by using appropriate relations between strain fluctuations and mechanical compliances. It is important to note that only isothermal strain fluctuations are accessible in PIMD simulations. A constant enthalpy simulation of the isomorphic classical representation would not translate into conserved enthalpy of the quantum crystal.

In principle, our method is closely related to a recently proposed PIMD scheme for constant-stress constant-temperature simulations. The special representation used here as well as omitting the thermostat included in the equations of motions in Ref. 24 anticipates to briefly review the final result. In order to do this, we represent the coordinate $R_{it}$ of particle $i$ at imaginary time $t$ as a product of a scaled coordinate $\tilde{r}_{it}$ and the time-dependent (symmetrical) matrix $h$, which contains the shape and the volume $V = \det h$ of the simulation cell:

$$R_{it} = h_{\alpha\beta} r_{it\beta}.$$  (1)

The values of $r_{ita}$ are constrained to values $0 \leq r_{ita} < 1$. The components of the metric tensor $G$ are defined as $G_{\alpha\beta} = h_{\alpha\mu} h_{\beta \nu}$ where summation over Greek indices enumerating spatial dimensions is implicitly assumed. It is then convenient to express the equations of motion for the scaled coordinates in reciprocal Fourier space, namely in terms of coordinates

$$\tilde{R}_{it\alpha} = \frac{1}{\sqrt{P}} \sum_{t=1}^{P} r_{it\alpha} \exp \left( \frac{2\pi i \omega t}{P} \right)$$  (2)

for which the motion of the free particles is diagonalized. Introducing $k_{a\mu} = 4 \pi m \sin^2(\pi \omega t/P)/(\beta\hbar)^2$, allows to represent the equations of motion in a rather condensed form:

$$m_{i\omega} \ddot{r}_{i\omega\mu} = \tilde{m}_{i\omega}(G^{-1})_{\mu\nu} \ddot{r}_{i\omega\nu} - k_{i\omega} r_{i\omega\mu} + \frac{1}{\sqrt{P}} \sum_{t} e^{2\pi i \omega t} \sum_{j \neq i} \frac{\partial v_{ij}}{\partial R_{ij\mu}} r_{j\mu} - r_{j\mu}$$  (3)

$$PW \dot{h}_{\mu
u} = \sum_{i\omega} \tilde{m}_{i\omega} \ddot{R}_{i\omega\mu} - \sum_{it} \frac{m_{i\omega} P^2}{\beta \hbar^2} (r_{ita} - r_{it-1\sigma})(R_{ita} - R_{it-1\sigma}) + \sum_{it} \sum_{j > i} \frac{\partial v_{ij}}{\partial R_{ij\mu}} R_{(ij)\mu} R_{(ij)\nu}$$  (4)

with $v_{ij}$ a two-particle interaction potential between particle $i$ and $j$ and $R_{(ij)t}$ the vector connecting particle $i$ and $j$ at imaginary time $t$ employing minimum image conventions.

Despite the well-known disadvantages of Langevin-type thermostats, correlation times turned out to be...
particular small when all degrees of freedom (including the geometry of the simulation cell) were weakly coupled to a friction force linear in velocity and to a corresponding random force. Chosing the damping term $\gamma$ of the Langevin dynamics to be $\gamma = 0.01 \, dt$ and $dt = 0.04 \, t_{\text{char}}$ with $t_{\text{char}}$ the (smallest) characteristic time-scale of the system, systematic errors were made much smaller than statistical errors. Moreover, the ergodicity problems, which is inherent to some PIMD algorithms, can be most easily overcome with a Langevin thermostat. The average “dynamic” kinetic energy $\langle T_{\text{dyn}} \rangle$ and the fluctuation of $T_{\text{dyn}}$ in the PIMD approach described above, are utterly sensitive to bad choices of $\gamma$ and $dt$. In the correct limit, one obtains $\langle T_{\text{dyn}} \rangle/N = dk_B TP/2$ per degree of freedom and the associated specific heat (fluctuation) $\langle \delta T_{\text{dyn}}^2 \rangle/N k_B T^2 P^2 = dk_B/2$ with $d$ the spatial dimension of the system. This sensitivity can be used to determine the accuracy of the simulation resulting in reliable thermodynamic expectation values of other observables. Note that only independent components of the Fourier transform $\hat{r}_\omega$ need to be thermostated and considered for the calculation of the dynamic kinetic energy.

### B. Dynamical information

Imaginary-time path-integral methods do not allow direct calculation of dynamical properties. While the complete dynamical information is obtained in imaginary-time correlation functions in principle, the inverse Laplace transform that one needs to carry out in order to assess real-time correlation functions is numerically unstable. A generalization of the PIMD method, the centroid molecular dynamics (CMD) method, appears to give a more direct link between exact quantum dynamics and CMD. The basic idea of CMD is to propagate the centroid molecular dynamics (CMD) method, invokes systematic errors in the partition function and observables that vanish proportionally to $1/(TP)^2$. It is therefore important to chose $P$ large enough so that quantum effects are well reflected. On the other hand, $P$ should not be too large, which would result in large statistical error bars.

In order to assess at what values of $TP$ one can expect convergence to the quantum limit, the average potential energy $\langle V_{\text{pot}} \rangle$ is calculated for various values of $P$ at the temperature $T = 300 \, \text{K}$. The results are shown in Fig. 1. For $PT > 1200 \, \text{K}$, extrapolation to the quantum limit is possible with correction in the order $1/(TP)^2$. Combinations satisfying $PT > 4, 800 \, \text{K}$ basically correspond to the quantum limit.

Depending on the property of interest, it is necessary to extrapolate to the quantum limit with a $1/P^2$ corrections. This concerns particularly structural data, such as lattice constants, which can be obtained with high resolution. Elastic constants and dynamical information, however, are plagued with relatively large statistical error bars. For these observables, statistical uncertainties are much larger than systematic deviations and results obtained with $PT > 2, 400 \, \text{K}$ are referred to as quantum limit.

The total number of atoms used in the simulations was $N = 1080$. The linear box dimensions typically are $24.9 \, \text{Å}$, $25.9 \, \text{Å}$, and $21.9 \, \text{Å}$ along the $a$, $b$, and $c$ axis, respectively. In order to obtain elastic constants with an accuracy of about 3 GPa, 60,000 MD steps of length 1 fs have to be performed, which takes about one day on an Intel II processor. For quantum simulations, the numerical effort has to be multiplied with Trotter number $P$.

### C. Model Specific Information

In the present simulation, $v_{ij}$ in Eqs. (3) corresponds to the BKS interaction potential between particles $i$ and $j$ including the Coulomb energy among other contributions. For the evaluation of the Ewald sum in arbitrarily shaped parallelepiped simulation cells, a recently proposed algorithm was used and constrained to symmetric matrices $h$ resulting in a 30% reduction of CPU time to evaluate the Ewald sum. The non-Coulombic interactions were cut off at a distance $r_c = 9.5 \, \text{Å}$.

In the following, it will be distinguished between classical and quantum mechanical results. Classical results are obtained by simply chosing $P = 1$ in a PIMD simulation. Exact quantum results require taking the limit $P \to \infty$ in principle. It is well known that the so-called primitive decomposition of the density matrix, upon which the PIMD algorithm is based, invokes systematic errors in the partition function and observables that vanish proportionally to $1/(TP)^2$. It is therefore important to chose $P$ large enough so that quantum effects are well reflected. On the other hand, $P$ should not be too large, which would result in large statistical error bars.

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### III. RESULTS
A. Structural Properties

Two temperature regimes are particularly interesting to study, namely room temperature and temperatures near absolute zero. We first start with a discussion of quantum effects at room temperature, \( T = 300 \text{ K} \). This temperature is already well below the Debye temperature \( T_D \) of quartz. \( T_D \) of \( \alpha \)-quartz as determined by specific heat measurements is a strongly temperature-dependent function:\[ T_D = 3500 \text{ K} \]. At \( T = 0 \), \( T_D \approx 550 \text{ K} \), while at room temperature \( T_D \approx 1,000 \text{ K} \). Some quantum effects can therefore be expected to be relatively strong at room temperature. In Fig. 2, one can see that the main quantum effect at room temperature is the quantum mechanical freezing of the Si-O bond. This freezing is reflected by the fact that the distribution \( p_{\text{SiO}}(r) \) of the Si-O bond is much broader for the quantum mechanical study than for the classical study (Fig. 2a). In fact, the quantum mechanical \( p_{\text{SiO}}(r) \) barely changes its form when the temperature is lowered further. This is an indication that Si-O bonds are in their quantum mechanical ground state. On the other hand, Si-O-Si bond angles as well as O-Si-O bond angles do not differ considerably between classical and PIMD simulations (Fig. 2b).

Fig. 3 and Fig. 4 show the effect of the quantum mechanical ionic motion on simple structural properties. The average Si-O bond length \( r_{\text{SiO}} \) is shown in Fig. 3 as a function of temperature, while the lattice constants \( a \) and \( c \) are shown in Fig. 3. In all cases, it is noticeable that the quantum mechanical values are larger than the classical equilibrium lengths. The effects are relatively small, but clearly within the resolution of the simulations. While \( r_{\text{SiO}} \) only differ by 0.19% at \( T = 150 \text{ K} \), the lattice constants differ by 0.35% in the case of both the \( a \) axis and \( c \) axis of \( \alpha \)-quartz. This means that the “excess” quantum volume can be attributed to both the SiO bond length and quantum fluctuations of the so-called rigid unit mode (RUM).

In the case of the lattice constants, Fig. 3b, direct comparison can be made to experimental data.\[ C_{\alpha \beta} = \frac{\partial^2 (V(T, c))/\partial c_{\alpha} \partial c_{\beta}}{V(T, c)} \] (7) where the derivative is evaluated at zero strain. At finite temperatures, it is not sufficient to generalize this expression by simply taking the thermal expectation value of the right hand side. It has been pointed out correctly that the free energy surface \( F(T, c) \) should be considered instead of \( V(T, c) \). This generalization leads to different estimators of the elastic constants when evaluated in the (NVT) ensemble. The main effect of this generalization is that fluctuations of the stress tensor need to be considered on top of the Born term described in Eq. 6. These fluctuations usually lead to a reduction of the elastic constants. Unlike classical fluctuation terms, quantum mechanically calculated terms will not vanish as the temperature approaches absolute zero. Among other effects, this will lead to different elastic constants for quantum mechanical and classical systems. In the case of silicates, however, it turns out that it is more efficient to calculate elastic constants \( C_{ij} \) by exploiting the

B. Elastic properties

Just like other properties can elastic constants be expected to differ between classical and quantum mechanical treatments. In order to calculate classical constants at zero temperature, it is sufficient to calculate the second derivative of the ground state (potential) energy with respect to the stress tensor, resulting in the so-called Born expression for elastic constants:\[ C_{\alpha \beta} = \frac{\partial^2 (V(T, c))/\partial c_{\alpha} \partial c_{\beta}}{V(T, c)} \] (7)
correlation function between $C_{ij}$ and the thermal fluctuations of the strain tensor.

Experimental, classical, and quantum mechanical elastic constants are compared in Fig. 3. Elastic constants can be expected to show larger (relative) quantum corrections than lattice constants and heat of formation. For quartz, the reduction of about 5 GPa in $C_{33}$ seems to be the most dramatic effect. At $T = 300$ K, classical and quantum mechanical elastic constants agree within the statistical error bars. Below 300 K, the classical $C_{33}$ shows a stronger temperature dependence than the quantum mechanical $C_{33}$. This effect should be taken into account when trying to optimize potential energy surfaces: $C_{33}$ predicted by the force field parameters for $T = 0$ K should be a little larger than $C_{33}$ measured at a temperature of 300 K. For other $C_{ij}$ the same comment applies in principle, but quantitatively, the effects are less dramatic.

C. Dynamical Properties

As a generic dynamical property we consider the (classical) inverse-mass weighted momentum autocorrelation function $C(t)$

$$C(t) = \sum_i m_i^{-1} \langle \vec{p}_i(t) \vec{p}_i(0) \rangle,$$  \hspace{1cm} (8)

where $t$ denotes the real time. $C(t)$’s Fourier transform $\tilde{C}(\omega)$ can be used to define an effective density of states $g_{\text{eff}}(\nu)$

$$g_{\text{eff}}(\nu) = \frac{\tilde{C}(2\pi\nu)}{N k_B T n(\beta h\nu)}$$  \hspace{1cm} (9)

with $n(\beta h\nu)$ being introduced in Eq. (3). $g_{\text{eff}}(\nu)$ is identical with the real density of states (DOS) if the harmonic approximation is valid. $\tilde{C}(\omega)$ and hence the effective DOS can be exactly related to the imaginary-time correlation function $G(\tau)$

$$G(\tau) = \sum_i m_i \left( \langle \vec{R}_i(\tau) - \vec{R}_i(0) \rangle \right)^2$$  \hspace{1cm} (10)

via the two-sided Laplace transform

$$G(\tau) = \int_{-\infty}^{\infty} d\omega \exp(-\beta h\omega/2) \times \frac{\tilde{C}(\omega)}{\omega^2} \left[ \cosh \left( \frac{\beta - \tau}{2} \right) - \cosh \frac{h\omega}{2} \right].$$  \hspace{1cm} (11)

Note that the imaginary time $\tau$ has to be considered within the interval $0 \leq \tau < \beta$. Outside of this interval, imaginary-time correlation functions are repeated periodically.

Eq. (11) is useful to check the validity of the centroid molecular dynamics (CMD) method and hence to establish the validity of spectral functions as obtained by CMD. If $C(t)$ is determined in terms of the mass-weighted autocorrelation function of the centroid velocities and use is made of Eq. (11), the effective DOS and hence $G(\tau)$ can be estimated in terms of centroid dynamics. If CMD is applicable, $G(\tau)$ as obtained by direct sampling and $G(\tau)$ as estimated via CMD have to agree. As shown in Fig. 3 the agreement is perfect within our statistical error bars for α-quartz at very low temperatures. Of course, this agreement could be expected as the dynamics are dominated by the harmonic interactions unlike the thermal expansion coefficients. Note that a purely classical simulation leads to a similarly good agreement. CMD and classical velocity autocorrelation functions can barely be distinguished in the case of quartz.

Fig. 3 shows the density of states as calculated via the centroid PIMD. Of course, a degree of (meaningful) complexity in a spectrum such as shown in Fig. 3 can never be obtained by inverting imaginary-time correlation functions as shown in Fig. 3. Thus, centroid PIMD are a useful tool to obtain DOS of silica.

IV. CONCLUSIONS

This study shows that path integral molecular dynamics (PIMD) are an efficient tool to calculate low-temperature properties of solids even if the complexity is larger than in rare gas crystals or other monoatomic solids. PIMD turns out to be particulary useful (as compared to path-integral Monte Carlo) when long-range forces have to be evaluated such as it is the case for the simulations of silica. Structural properties can be evaluated with high resolution and the shift from properties that are obtained if atomic motion is treated classically to the “real” quantum mechanical properties can be assessed. This shift can also be calculated for elastic constants, which are notoriously hard to compute even in classical simulations.

The result of the PIMD simulations anticipate that path integral techniques may not only become an important way of evaluating the merits and failures of potential energy surfaces, but PIMD might give valuable input to construct reliable model potentials. Here, the PIMD calculations of the thermomechanical properties of α-quartz were based on the BKS potential. The construction of the BKS potential was pioneering in the sense that ab-initio calculations were combined with bulk properties in order to fit the free model parameters. In the latter part, lattice constants and elastic constants were calculated for a classical system at $T = 0$ K from the (fit) parameters and adjusted such that agreement with experimental “quantum mechanical” (finite temperatures) data was optimum. The PIMD results in combination with the classical MD results presented in this paper, show that this part of adjusting the parameters of the
BKS potential allows for further optimization. Of course, one can not necessarily expect to find a two-body potential energy surface for silica that describes interactions much better than the BKS potential.

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FIG. 1. Average potential energy \( \langle V_{\text{pot}} \rangle \) for different Trotter numbers, \( P = 2^n \) with \( n = 0, \ldots, 5 \), at \( T = 300 \) K. Straight line is a fit for large \( P \) including corrections to the asymptotic quantum value in the order of \( 1/P^2 \). Error bars smaller than 1 k_B K.

FIG. 2. a) Probability density \( p(r) \) to find an oxygen atom in a distance \( r \) from a silicon atom. b) O-Si-O (left) and Si-O-Si (right) bond angle distribution function \( p(\alpha) \). Solid lines reflect classical simulations, dashed lines represent quantum mechanical simulations. Temperature \( T = 300 \) K.

FIG. 3. Average Si-O bond length \( \langle r_{\text{SiO}} \rangle \) as a function of temperature. A linear fit of the classical data indicates an average equilibrium distance of 1.6017 Å.

FIG. 4. Lattice constants of \( \alpha \)-quartz at ambient pressure as a function of temperature. a) Experimental values for the \( a \)-axis are shifted to larger values by 0.06 Å. b) Experimental values for the \( c \)-axis are shifted to larger values by 0.07 Å. Error bars in all cases smaller than 100 fm.
FIG. 5. O-Si-O (left) and Si-O-Si (right) bond angle distribution at temperature $T = 80$ K.

FIG. 6. Mean bond angle as a function of temperature for classical (straight line) and quantum mechanical (circles) simulations. a) Si-O-Si bond. b) O-Si-O bond.

FIG. 7. Various elastic constants. Experimental data is taken from Carpenter et al. (1998). Open symbols refer to classical simulations, filled symbols to PIMD simulations. Statistical error bars are about 2 GPa.

FIG. 8. The imaginary-time correlation function $G(\tau)$ at $T = 80$ K as obtained directly (points) and via the centroid PIMD method.

FIG. 9. The density of states $g(\nu)$ as predicted by the centroid PIMD method. $g(\nu)$ serves as an input spectrum to previous figure. Dotted line is drawn to guide the eye.