Reply to the report of Dr Wehinger

We would like to thank Dr Wehinger for careful reading of the manuscript and his positive opinion on our work.

> The authors of the manuscript "High Efficiency Configuration Space Sampling – probing the distribution of available states" present a new method for studying lattice dynamics at finite temperatures. Their approach is based on configuration sampling the distribution of available states using the Metropolis-Hasting algorithm with a prior probability distribution derived from harmonic lattice dynamics. The authors compute anharmonic phonon dispersions and lifetimes for 3C-SiC to validate their approach and claim high computational performance due to a large observed acceptance ratio. The idea is highly original and I expect significant impact for the study of thermal properties at finite temperatures in large crystalline systems containing many atoms per unit cells. In order to fully convince the reader and justify publication in SciPost Physics, I recommend the authors to address and clarify the following:

We would like to point out that the presented approach *does not* depend on strict harmonicity of the system. The Eq. (4) and its description (l. 78-87) explicitly point to the impact of the anharmonicity on the formulas used in the proposed method. In particular, the normality of the distribution is *not* impacted - since it originates from the Central Limit Theorem (CLT, Eq. 5). What may be influenced is the value of the mean and the variance of the distribution - which will skew the temperature scale and possibly diminish the fidelity of our approximation of the thermal equilibrium state. Since both referees missed this point we have expanded our explanation of this issue to make it more clear to the reader.

Additionally, while we use lattice dynamics as an example in the text, the potential applicability of the proposed method is broader - it may be useful in other places where we need to reproduce the configuration of the system of atoms in thermal equilibrium in non-zero temperature. This fact is mentioned in the abstract but we will expand the conclusions by mentioning it there as well.

> 1. The lattice dynamics of 3C-SiC at room temperature can be described fairly well by the harmonic approximation. It seems thus no big surprise that a prior probability distribution derived from harmonic lattice dynamics converges successfully and quickly. But how well does it work for a more anharmonic situation? Although the chosen potentials might not be accurate close to melting it would be a very nice illustration to compare the dispersions and lifetimes to molecular dynamics simulations at a temperature where anharmonic effects are

more important.

Indeed, the chosen system is not strongly anharmonic at T=300K. But still there is enough anharmonicity in the model to produce 5ps phonon lifetimes plotted in Fig. 6. Also, the Tersoff potential selected for the study is *not* a simplistic, harmonic, two-body potential. It is a published, effective model of interactions in the Si-C compounds.

We would like to stress that the closeness of the prior distribution to the target (Figs 3 and 4) originates from the size of the system and careful selection of the prior generating algorithm (Eq. 6 and description in l. 172-183). As we noted in the reply to the first referee the extreme cases of anharmonicity dominating the right hand side of the Eq. 4 for all, or most coordinates may be beyond the direct applicability of the proposed method. To illustrate the point, we have added to Figures 3, 4, 5, and 6 the calculations performed for higher temperatures (up to T=2000K) closer to the melting point of 3C-SiC demonstrating effectiveness of the proposed approach even in high temperatures.

2. The performance of the new approach is based on comparing its acceptance ratio to molecular dynamics simulations. How do actual computation times compare? How does the performance (computation time) scale with system size including the possibility to run calculation in parallel on many cores?

The computational cost is essentially proportional to the number of requested configurations plus necessary burn-in samples (1-10, can be limited to 1-2 with careful selection of initial displacement variation). Due to the details of the Metropolis-Hastings algorithm this cost is *independent* of the acceptance ratio. Low acceptance ratio leads to low quality of the generated distribution, not a direct increase in computational cost. This increase stems from the fact that with low acceptance more samples are required for the reasonable fidelity of the produced distribution. In comparison with MD calculations, each generated configuration is equivalent to one time step in trajectory. However, in case of the DFT-based calculations, the MD procedure can be optimized by starting each step from the charge density/wave functions converged in the previous step. Due to the fact that samples generated by HECSS are independent, this optimization is not easily available in DFT-based calculations. This amounts to approximately twice as many electronic SCF steps per evaluated configuration. Thus, n-configurations HECSS run is equivalent to approximately 2*(n+10) time steps of the MD calculation. In our experience this is not enough to provide even single, well-thermalized sample for n<500.

Regarding the parallel computation: In current implementation each configuration evaluation may be run on multiple cores but the sample generation is strictly serial. The near-independence of generated samples provides opportunity for future splitting of the computation to multiple processes. Naturally, each temperature scan may be run as a separate process with full linear scaling.

We will add analysis of the computational cost of the HECSS approach to the

final paragraph of the text.

> 3. Presentation. Title and abstract suggest application of the method to a wild variety of problems in solid state physics. However, such are mentioned only marginally in the conclusions while the main text fully focuses on the application to lattice dynamics. Experts in lattice dynamics may thus overlook this work and its relevance if not highlighted better. At several points the manuscript would profit from more quantitative statements.

We will expand the abstract to better reflect our focus - which is indeed, at this moment, on lattice dynamics applications. The other applications mentioned in the abstract are our suggestions of other fields where this type of procedure may be beneficial.

> Lines 80-81: Limitations and applications should be discussed in more details. Lines 102-103: Phase transitions are excluded by the "reasonable" class. This should me mentioned and the application of the approach to different kind of phase transitions could be addressed.

Following the comment of the first referee we have expanded the description of probable limitations of the proposed method (phase transitions, highly anharmonic systems).

> Lines 114-115: "too wild" and "very quick" should be quantified.
>
> Lines 136- 137: "barely noticeable" and "hardly visible" obviously depend on how the data is plotted. Please quantify.

We have replaced these imprecise phrases with quantitative description showing the speed of convergence and cited the appropriate literature.

> Figs. 1 and 2. correlations between E_kvar and E_pvar could be discussed.

The correlation between variances of the kinetic and potential distribution comes directly from energy conservation and statistical mechanics. Both energies are part of the Hamiltonian and sum up to the total energy. Thus, due to the energy conservation their variances should match. We have added the appropriate sentence to the discussion at the end of section 2.

> Lines 186-189: Asymptotic production of target distribution for any non-vanishing prior distribution requires a citation.

Appropriate citation has been added to the list of references.

> Lines 213-214: Please explain why parameters are independent and their values not critical. Are there limitations?

The independence from the system (supercell) size stems from the connection with the displacement distribution - it is our conclusion drawn from the experience gained during the development of the HECSS scheme. If the interactions are reproduced reasonably well in the small supercell (e.g. single crystallographic unit cell) the average size of thermal displacement is expected to be the same as in larger supercell due to the same energy per degree of freedom (i.e. temperature) and very similar shape of the potential. The independence and the practical ranges of the parameters cited in the text are derived from the multiple tests run during the development of the HECSS code. We have added a sentence explaining this property and rephrased the surrounding text to make this issue more clear to the reader.

> Figures 5 and 6 should be discussed in more detail. Agreement and differences need to be pointed out. Fig. 5 is confusing. It's caption suggest that molecular dynamics was used to extract harmonic phonon frequencies, while the text states that higher order (anharmonic) force constants were extracted. It would be nice to compare harmonic phonon frequencies to both anharmonic phonon frequencies obtained from molecular dynamics and from the new method and discuss agreement and differences in detail for at least two different temperatures.

The phonon frequencies presented in Fig. 5 are derived by fitting of a third order *anharmonic* model to both datasets and the frequencies are derived from this model. The lifetimes from the Fig. 6 are obtained from the same model using ALAMODE to compute anharmonic self-energy and phonon lifetimes from the third order coefficients in the fit (using relaxation time approximation). We have corrected a misleading description of Figs 5 and 6 and expanded the description to make the point clear. We have also included the RMS differences between phonon frequencies derived by both methods.

> Fig. 6 is lacking information on lifetimes of the acoustic branches with small momenta and small energies close to the Γ-point. It would be nice to discuss convergence and numerical limitations for these.

The access to the vicinity of the zone-center is limited by the supercell size used in the calculation. The closest point provided by the supercell used in the paper (5x5x5, 1000 atoms) and reciprocal space sampling grid (20x20x20) is located at 1/10 of the zone size from the center. All data between this point and the zone center are interpolated from the fitted force constant matrices in real space. We will add information about the reciprocal space sampling to the text. Additionally we have expanded the presented data to include more temperatures: 100K 600K and 2000K.

> Both figures are very difficult to read because they are small and contain too much data. Splitting into sub-panels where the same number of samples are compared could help.

Figure 5 is intended to show small difference between frequencies computed from

both data sets. We agree that the presentation in both Fig. 5 and 6 will benefit from such split and we have replaced both figures by separate panels containing data sets of the same size. We have also added additional temperatures - as mentioned above. The description has been modified appropriately.

> In summary, the presented approach is highly innovative and worth to be published but the presentation needs to be improved to make it convincing.

We hope that the above explanations and corrections to the text make our paper convincing and clarify all the issues raised by Dr Wehinger.