A novel Bayesian approach to the computation of the configurational density of states

Felipe Moreno\textsuperscript{a}, Sergio Davis\textsuperscript{b,a}, Joaquín Peralta\textsuperscript{a}

\textsuperscript{a}Departamento de Física, Facultad de Ciencias Exactas, Universidad Andrés Bello, Sazié 2212, Santiago, Chile.
\textsuperscript{b}Research Center in the Intersection of Plasma Physics, Matter and Complexity (P2mc), Comisión Chilena de Energía Nuclear, Casilla 188-D, Santiago 7600713, Chile.

Abstract

In this work we develop and implement a novel Bayesian method for computing the DOS of a system. This method is based on the use of a test function with adjustable parameters and we use Bayes theorem to find the best parameters given a certain number of measurements done on the system. This measurements can be done in any ensemble defined by a distribution function. We found that the algorithm can find the DOS in a reasonable amount of time, and that if the test function is suitable enough, the DOS found by the algorithm is very close to the true DOS.

Keywords: Density of States, Bayes Theorem, Algorithm

1. Introduction

The density of states (DOS), on its different flavors, such like energy, vibrational, configurational, among others [1], is essentially the number of states per unit of energy. The configurational density of states, defined for a system with degrees of freedom $x$ and potential energy $\Phi(x)$ is given by

$$D(\phi) := \int dx \delta(\Phi(x) - \phi).$$ (1)

In physics and chemistry this DOS have an outstanding importance, because a large amount of information can be obtained from it. In spite of the enormous success in characterizing physical and chemical quantities based on the DOS [2–7], it is not a easy to obtain function, which reduce its use, in spite of the their characteristics, on multiples research areas [8–10].

Different approaches has been implemented to find the DOS for a large variety of systems [11–14]. Nowadays one of the most successful techniques correspond to determine the DOS is the one based in Wang Landau algorithm [14], this technique is based on flat-histogram procedure and have been showed that plenty of programming techniques and improvements has been implemented during last decades [15–17]. However it is not easy to calculate nor programming, and is even more difficult to apply on specific scenarios, such like ab-initio.

While Wang-Landau has been very popular this time, there are different techniques for calculating DOS that are still in use, such as parallel tempering [18], metadynamics [19–21], and other techniques based on flat histograms [9, 22]. In most of these cases, solution are focused on specific problems, and not always cover the variety of cases where DOS could be used. Motivated on this, and also in the incorporation of most general statistical techniques, we worked in a new methodology to determine the DOS.

In this work we present a novel procedure to obtain the energetic density of states (DOS) for solid materials, based on Bayesian method. Here we develop this novel technique by: i) incorporate the Bayesian Theorem on the procedure, ii) develop a modular implementation on a wide and popular programming language as Python3, and iii) the speed-up of certain function using C language.

Email addresses: f.moreno.munoz@gmail.com (Felipe Moreno), sergio.davis@cchen.cl (Sergio Davis), joaquin.peralta@unab.cl (Joaquín Peralta)

Preprint submitted to Elsevier

December 28, 2021
In what follows we present the Algorithm description which connect the Bayesian theorem and the DOS (sec. 2). On section 3 a brief description of the implementation of the algorithm is presented using Python programming language. Section 4 present cases of study for different scenarios, such like classical solid structure using a Lennard-Jones interatomic potential, and the Ising model. Finally on section 5 conclusions and scope of our work is discussed.

2. Algorithm

Suppose the DOS of a system is completely determined by \( m \) parameters \( \theta = (\theta_1, \ldots, \theta_m) \)

\[
D(\phi) = D(\phi; \theta).
\]  

(2)

The probability that an ensemble \( S \) has a certain energy \( \phi \) is

\[
P(\phi; S|\theta) = \frac{\rho(\phi; S) D(\phi; \theta)}{Z(\theta; S)}
\]  

(3)

where \( \rho(\phi; S) \) is the distribution that defines the ensemble \( S \) and \( Z(\theta; S) \) is the partition function defined by

\[
Z(\theta; S) = \int d\phi \rho(\phi; S) D(\phi; \theta).
\]  

(4)

Suppose we make \( n \) measurements of the ensemble energy, obtaining \( \phi_1, \ldots, \phi_n \). We want to know what is the most probable values of the parameters \( \theta \) compatible with those measurements. We accomplish this by computing the maximum of \( P(\theta|\phi_1, \ldots, \phi_n; S) \). In practice, it is better to compute the maximum of the logarithm of \( P(\theta|\phi_1, \ldots, \phi_n; S) \), that is,

\[
\frac{\partial}{\partial \theta_k} \ln P(\theta|\phi_1, \ldots, \phi_n; S) = 0 \quad k = 1, \ldots, m.
\]  

(5)

Because the measurements are considered to be statistically independent, we have

\[
P(\phi_1, \ldots, \phi_n|\theta, S) = \prod_{i=1}^{n} \frac{\rho(\phi_i; S) D(\phi_i; \theta)}{Z(\theta; S)}
\]  

(6)

and, by using Bayes theorem [23] we have

\[
P(\theta|\phi_1, \ldots, \phi_n; S) = \frac{P(\theta|I_0)P(\phi_1, \ldots, \phi_n|\theta, S)}{P(\phi_1, \ldots, \phi_n; S)}
\]  

\[
= \frac{P(\theta|I_0)}{P(\phi_1, \ldots, \phi_n; S)} \prod_{i=1}^{n} \frac{\rho(\phi_i; S) D(\phi_i; \theta)}{Z(\theta; S)}
\]  

(7)

\[
= \frac{1}{\eta} P(\theta|I_0) \prod_{i=1}^{n} \frac{D(\phi_i; \theta)}{Z(\theta; S)^n}
\]

where

\[
\eta := \frac{\prod_{i=1}^{n} \rho(\phi_i; S)}{P(\phi_1, \ldots, \phi_n|I_0)}
\]  

(8)

is an irrelevant normalization constant that does not depend on \( \theta \). In this way, Eq. 5 can be written as

\[
\frac{\partial}{\partial \theta_k} \ln P(\theta|\phi_1, \ldots, \phi_n; S) = \frac{\partial}{\partial \theta_k} \ln P(\theta|I_0) + \sum_{i=1}^{n} \frac{\partial}{\partial \theta_k} \ln D(\phi_i; \theta) - n \frac{\partial}{\partial \theta_k} \ln Z(\theta; S) = 0.
\]  

(9)

In the limit \( n \to \infty \) the first term on the right-hand side of Eq. 9 is negligible, and Eq. 5 becomes

\[
\frac{\partial}{\partial \theta_k} \ln Z(\theta; S) = \frac{1}{n} \sum_{i=1}^{n} \frac{\partial}{\partial \theta_k} \ln D(\phi_i; \theta)
\]  

(10)
for $k = 1, \ldots, m$. Notice that the right-hand side is the average of a known function of the measurements, while the left-hand side is given by

$$
\frac{\partial}{\partial \theta_k} \ln Z(\theta; S) = \frac{1}{Z(\theta; S)} \int d\phi \rho(\phi; S) \frac{\partial}{\partial \theta_k} D(\phi; \theta)
$$

$$
= \frac{1}{Z(\theta)} \int d\phi \rho(\phi; S) D(\phi; \theta) \frac{\partial}{\partial \theta_k} \ln D(\phi; \theta)
$$

$$
= \left\langle \frac{\partial}{\partial \theta_k} \ln D(\phi; \theta) \right\rangle_S,
$$

(11)

that is, the expectation value over the ensemble of the same function that is averaged on the right-hand side. In other words, we have that the condition that fixes $\theta$ is simply

$$
\left\langle \frac{\partial}{\partial \theta_k} \ln D(\phi; \theta) \right\rangle_S = \frac{\partial}{\partial \theta_k} \ln D(\phi; \theta)
$$

(12)

for $k = 1, \ldots, m$. This condition can be understood as the validity of the law of large numbers, namely the identification of the expected value with the data average, for the logarithmic derivatives of the density of states.

A straightforward generalization is to consider $r$ groups of $n_1, \ldots, n_r$ measurements obtained from different ensembles $S_1, \ldots, S_r$, respectively. Then Eq. 7 generalizes to

$$
P(\theta|\phi_1, \ldots, \phi_r; S_1, \ldots, S_r) = \frac{1}{\eta} P(\theta) \prod_{j=1}^{N} D(\phi_j; \theta) \prod_{S} \left[ Z(\theta; S) \right]^{n_S}
$$

(13)

where $N = \sum_{j=1}^{r} n_j$ is the total number of measurements, and Eq. 12 generalizes to

$$
\sum_{j=1}^{r} \frac{n_j}{N} \left\langle \frac{\partial}{\partial \theta_k} \ln D(\phi; \theta) \right\rangle_{S_j} = \frac{\partial}{\partial \theta_k} \ln D(\phi; \theta)
$$

(14)

for $k = 1, \ldots, m$ where the average in the right hand side is performed over all $N$ measurements. This algorithm is based on the solution of Eq. 14 by numerical methods. An equivalent problem is to search for the global minimum of

$$
\epsilon^2(\theta) = \sum_{k=1}^{m} \left[ \sum_{j=1}^{r} \frac{n_j}{N} \left\langle \frac{\partial}{\partial \theta_k} \ln D(\phi; \theta) \right\rangle_{S_j} \right]^2 - \frac{\partial}{\partial \theta_k} \ln D(\phi; \theta)
$$

(15)

by using numerical minimization methods such as particle swarm optimization (PSO) [24].

Now we can formulate a practical method of computing the DOS, using Eq. 15. Firstly, we select a set of canonical ensembles $S_1, \ldots, S_r$ such that

$$
\rho(\phi; S_j) \propto \exp(-\beta_j \phi)
$$

and we take $n_j$ samples of energy respectively. The ensemble information ($\beta_j$) and the measurements ($\phi_i$) are stored. Secondly, we choose a suitable function $\ln D(\phi; \theta)$ and then we run a minimization algorithm on the sampled data in order to find the global minimum of $\epsilon^2(\theta)$. Once the global minimum has been found, the parameters $\theta$ that minimize $\epsilon^2(\theta)$ are the ones that maximize the probability that $D(\phi; \theta)$ is the true DOS, within the chosen parametrization. If the function chosen is suitable enough, we expect this function to be very close to the true DOS.

Alternatively, we could have chosen a different set of ensembles, for instance, the microcanonical configurational ensemble

$$
\rho(\phi; S_j) \propto (E_j - \phi)^{d-1}
$$

for different total energies $E_1, \ldots, E_r$ where $d$ is the number of spatial dimensions.
3. Implementation

The algorithm consists of two parts. The first one is to generate measurements of the ensemble energy. We do this by using a canonical Monte Carlo Metropolis algorithm. We set an initial state \( x = (x_1, \ldots, x_N) \) and we propose a transition to a new state \( x' \) which is accepted with probability

\[
P(x \rightarrow x' | \beta) = \min \left( 1, e^{-\beta(\Phi(x') - \Phi(x))} \right)
\]

where \( \Phi(x) \) is the configurational energy of state \( x \). We vary \( \beta \) in order to produce data for different ensembles. We take samples of the ensemble energy after a certain number of calibration steps have been performed following each variation of \( \beta \). This part of the algorithm will generate two files, one with the set of temperatures \( \beta_j \) that define each ensemble, and one with the sampled energies.

The second part of the algorithm is to run a PSO algorithm on the sampled data in order to find the global minimum of \( \epsilon^2(\theta) \). Since the computation of \( \epsilon^2 \) is the computationally expensive part of the algorithm, it has been coded in C++ and loaded as a library into a more user-friendly Python code.

Furthermore, we can speed up the minimization by considering a very common special case. Suppose that \( \ln D(\phi, \theta) \) depends linearly on the parameters \( \theta \), that is

\[
\ln D(\phi; \theta) = \sum_{k=1}^{m} \theta_k f_k(\phi)
\]

where we can interpret the set of functions \( \{f_1(\phi), \ldots, f_m(\phi)\} \) as a basis for the representation of the density of states. Inserting this into Eq. 15 we obtain

\[
\epsilon^2(\theta) = \sum_{k=1}^{m} \left( \frac{1}{n_j} \sum_{j=1}^{r_j} (f_k(\phi))_{S_j} - \overline{f_k(\phi)} \right)^2,
\]

where the terms \( \overline{f_k(\phi)} \) do not depend on \( \theta \) thus they will only need to be computed once. Since these are the only terms that depend on the sampled data, we can make the minimization time independent of the size of this data.

To estimate the statistical error of the DOS reconstruction, we propose the use of the Bayesian information criteria (BIC) [25], which is defined by:

\[
\text{BIC} := -2 \ln P(\phi_1, \ldots, \phi_N; \theta) + m \ln N
\]

and such that we should prefer the model with the lowest BIC to reduce the error. By using Eq. 6 we have

\[
\text{BIC} = -2N(\ln \rho(\phi; S) + \ln D(\phi; \theta) - \ln Z(\theta; S)) + m \ln N.
\]

Because the first term inside the parenthesis does not depend on the parameterization \( \theta \) we can instead compare two models \( D_1(\phi; \theta_1) \) and \( D_2(\phi; \theta_2) \) for the same set of ensembles and same data through the quantity

\[
\text{BIC}^* = -2 \left( N \ln D(\phi; \theta) - \sum_{j=1}^{r} n_j \ln Z(\theta; S_j) \right) + m \ln N.
\]

4. Results

The algorithm and implementation have been tested using a variety of systems in order to evaluate the accuracy of the suggested methodology.
4.1. Harmonic Oscillator
We consider a system of $N = 100$ identical harmonic oscillators,

$$\Phi(x) = \frac{1}{2} m \omega^2 \sum_{i=1}^{N} x_i^2.$$  \hspace{1cm} (22)

Instead of $\beta$ we have used $k_B T = \beta^{-1}$ in the range $k_B T \in [0.05, 5]$ at steps $\Delta (k_B T) = 0.05$. We consider the energy of the last 1000 steps of simulation—in a total of 10,000—for each $k_B T$. That is, we produce $r = 100$ values of $k_B T$ and $N = 100,000$ values of energy $\phi$.

Next, we chose the following test function with one parameter ($m = 1$),

$$\ln D(\phi; \theta) = \theta_1 \ln \phi.$$  \hspace{1cm} (23)

![Figure 1: Configurational DOS for a system of $N=100$ classical harmonic oscillators.](image)

We run the PSO algorithm on this data using 1760 particles and after 37 iterations we found that $\theta_1 = 49.001$, which closely matches the analytical result

$$D(\phi) \propto \phi^{N/2 - 1}.$$  

The results for this case are presented on figure 1, we observe an excellent agreement with the WL algorithm result.

4.2. Ising model
The Ising model is a well-known model of spins. The model consists in a lattice filled with spins that can take values $\sigma = \pm 1$. The model energy is computed according to

$$\phi = -J \sum_{(i,j)} \delta(\sigma_i, \sigma_j).$$  \hspace{1cm} (24)

where the sum is over adjacent pairs and $\delta(\sigma_i, \sigma_j)$ is 1 if $\sigma_i = \sigma_j$ and 0 otherwise. We use an Ising model on a $10 \times 10$ lattice and we approximate the DOS using two 1-parameter test functions. Since the DOS is defined up to a constant, we require that the test functions vanish at $\phi = \pm 200J$ which are the energies less populated. The test functions will be

$$\log D_1(\phi; \theta) = \theta_1 \left[ \left( \frac{\phi}{200} \right)^2 - 1 \right]$$  \hspace{1cm} (25)

$$\log D_2(\phi; \theta) = \theta_1 \cos \left( \frac{\phi}{2 \cdot 200} \right)$$  \hspace{1cm} (26)
We found the parameters $\theta_1 = -69.2799$ for the first function and $\theta_1 = 67.1554$ for the second one. The BIC is smaller for the cosine function $3.40277 \times 10^7 < 3.41584 \times 10^7$. The results for this case are presented on figure 2, we observe a better agreement with WL algorithm on the function with the lower BIC value.

![Figure 2: Configurational DOS for an Ising system of 100 spins on a $10 \times 10$ lattice using a quadratic and a cosine approximation for $\ln D(\phi)$.](image)

### 4.3. Lennard-Jones

Finally, we study a system that needs 2 parameters to get a good approximation. A Lennard–Jones gas is a gas of particles whose interaction energy is

$$\phi = \sum_{i,j} 4\varepsilon \left( \frac{\sigma}{r_{ij}} \right)^6 - \left( \frac{\sigma}{r_{ij}} \right)^{12},$$

where the sum is over every pair. For this system we consider the addition of a logarithm and a linear function.

$$\log D(\phi, \theta) = \theta_1 \log(\phi - \phi_0) + \theta_2 \phi$$

where $\phi_0$ is the minimum energy.

We found $\theta_1 = 1.52994 \times 10^2$ and $\theta_2 = 1.09103$. The drawback here is that this model is unable to produce the phase transition. In spite of this, as we can observe on figure 3, there is a clear insight in the figure whit a results that behave different on the two main branches of the WL algorithm. For energies lower than -530, the Bayesian estimation is above the WL approximation. On the other side, with energies above the -530 the Bayesian estimation is below the WL results. This suggest that our model it could be splitted on different branches when we know beforehand about the presence of a phase transition.

### 5. Conclusions

We have presented a new technique to determine the Density of States. Different simulation examples have been used: Ising model, Lenard-Jones, and classical harmonic oscillator. Our results shows a good agreement with the known theoretical results. Moreover this methodology shows an improvement on computational efforts to be required to determine the DOS. The requirement of an input function, its an strength when some insights are known beforehand, otherwise a large functional base can always be used. If the functional form is improved the BIC error procedure will return the most effective evaluation of the DOS.
Figure 3: Configurational DOS for a Lennard-Jones system of 120 particles assuming \( \log D(\phi) \) is of the form shown in Eq. 28.

6. Acknowledgments

FM thanks to Universidad Andrés Bello for providing the doctorate scholarship and acknowledges funding from ANID BECAS/DOCTORADO NACIONAL 21212267. SD acknowledges partial funding from ANID PIA ACT172101 grant. Computational work was supported by the supercomputing infrastructures of the NLHPC (ECM-02), and FENIX (UNAB).

References

[1] W.A. Harrison. *Electronic Structure and the Properties of Solids: The Physics of the Chemical Bond*. Dover Books on Physics. Dover Publications, 1989.
[2] C. J. Gommes, Y. Jiao, and S. Torquato. Density of states for a specified correlation function and the energy landscape. *Phys. Rev. Lett.*, 108:080601, Feb 2012.
[3] P. Sarker, T. Harrington, C. Toher, C. Oses, M. Samiee, J.-P. Maria, D. W. Brenner, K. S. Vecchio, and S. Curturolo. High-entropy high-hardness metal carbides discovered by entropy descriptors. *Nature Communications*, 9:1–10, 2018.
[4] E. J. Garboczi and M. F. Thorpe. Density of states for random-central-force elastic networks. *Phys. Rev. B*, 32:4513–4518, Oct 1985.
[5] John C. Mauro, Roger J. Loucks, Jitendra Balakrishnan, and Srikanth Raghavan. Monte carlo method for computing density of states and quench probability of potential energy and enthalpy landscapes. *The Journal of Chemical Physics*, 126(19):194103, 2007.
[6] S.-Q. Yu, J.-B. Wang, D. Ding, S.R. Johnson, D. Vasileska, and Y.-H. Zhang. Impact of electronic density of states on electroluminescence refrigeration. *Solid-State Electronics*, 51(10):1387–1390, 2007. Special Issue: Papers Selected from the NGC2007 Conference.
[7] N. Nakai, P. Miranović, M. Ichioka, and K. Machida. Theoretical study on the field dependence of the zero energy density of states in an anisotropic gap superconductors. *Journal of Physics and Chemistry of Solids*, 66(8):1362–1364, 2005. Proceedings of the ISSP International Symposium (ISSP-9)on Quantum Condensed System.
[8] Helge Rosé, Werner Ebeling, and Torsten Asselmeyer. The density of states — a measure of the difficulty of optimisation problems. In Hans-Michael Voigt, Werner Ebeling, Ingo Rechenberg, and Hans-Paul Schwefel, editors, *Parallel Problem Solving from Nature — PPSN IV*, pages 208–217, Berlin, Heidelberg, 1996. Springer Berlin Heidelberg.
[9] N. Rathore, T. A. Knotts IV, and J. J. de Pablo. Configurational temperature density of states simulations of proteins. *Biophys. J.*, 85:3963–3968, 2003.
[10] G. J. Rodgers and A. J. Bray. Density of states of a sparse random matrix. *Phys. Rev. B*, 37:3557–3562, Mar 1988.
[11] M S Methfessel, M H Bohn, and F M Mueller. Analytic-quadratic method of calculating the density of states. *Journal of Physics C: Solid State Physics*, 16:L949–L954, 09 1983.
[12] Hainam Do and Richard J. Wheatley. Density of states partitioning method for calculating the free energy of solids. *Journal of Chemical Theory and Computation*, 9(1):165–171, 2013. PMID: 26589019.
[13] Thomas Aquino Ariasoca, Sholihun, and Iman Santoso. Trotter-suzuki-time propagation method for calculating the density of states of disordered graphene. *Computational Materials Science*, 156:434–440, 2019.
[14] F. Wang and D. P. Landau. Efficient, multiple-range random walk algorithm to calculate the density of states. *Phys. Rev. Lett.*, 86:2050–2053, 2001.
[15] P. Dayal, S. Trebst, S. Wessel, D. Wurtz, M. Troyer, S. Sahapandit, and S. N. Coppersmith. Performance limitations of flat-histogram methods. *Phys. Rev. Lett.*, 92:097201, Mar 2004.
[16] Thomas Prellberg and Jarosław Krawczyk. Flat histogram version of the pruned and enriched rosenbluth method. Phys. Rev. Lett., 92:120602, Mar 2004.

[17] Faming Liang. A theory on flat histogram monte carlo algorithms. Journal of Statistical Physics, 122:511–520, 01 2006.

[18] D. J. Earl and M. W. Deem. Parallel tempering: Theory, applications, and new perspectives. Phys. Chem. Chem. Phys., 7:3910–3916, 2005.

[19] C. Micheletti, A. Laio, and M. Parrinello. Reconstructing the density of states by history-dependent metadynamics. Phys. Rev. Lett., 92:170601, 2004.

[20] A. Laio and F. L. Gervasio. Metadynamics: a method to simulate rare events and reconstruct the free energy in biophysics, chemistry and materials science. Rep. Prog. Phys., 71:126601, 2008.

[21] A. Barducci, G. Bussi, and M. Parrinello. Well-tempered metadynamics: A smoothly converging and tunable free-energy method. Phys. Rev. Lett., 100:020603, 2008.

[22] N. Rathore, T. A. Knotts, and J. J. de Pablo. Density of states simulations of proteins. J. Chem. Phys., 118(9):4285–4290, 2003.

[23] D. S. Sivia and J. Skilling. Data Analysis: A Bayesian Tutorial. Oxford University Press, 2006.

[24] A. E. Olsson. Particle Swarm Optimization: Theory, techniques and applications. Nova Science Publishers, 2011.

[25] G. E. Schwarz. Estimating the dimension of a model. Ann. Statist., 6:461–464, 1978.

[26] M. Habeck. Bayesian reconstruction of the density of states. Phys. Rev. Lett., 98:200601, 2007.

[27] F. Moreno, S. Davis, C. Loyola, and J. Peralta. Ordered metastable states in the Potts model and their connection with the superheated solid state. Phys. A, 509:361–368, 2018.

[28] C. Farias and S. Davis. Multiple metastable states in an off-lattice Potts model. Phys. A, 581:126215, 2021.

[29] S. Davis, J. Jain, and B. Bora. Computational statistical mechanics of a confined, three-dimensional Coulomb gas. Phys. Rev. E, 102:042137, 2020.