

An Undergraduate Review of Path Integral Molecular Dynamics

H. W. Sullivan¹*Dept. of Chemical Engineering, University of Utah*

(Dated: 19 December 2022)

Self-assembly and structural ordering is a complex, emergent property of liquids that is intimately related to macroscopic and microscopic phenomenon.¹ A foremost objective of modern research in liquid state physics is the development and optimization of computer simulations that can accurately predict the behavior of materials from the atomic scale for any arbitrary system, and we expect such models to closely agree with experimental measurements of macroscopic behavior (PV diagrams, heat capacity, etc) and microscopic behavior (pair correlation functions, diffusion coefficients, etc).² Common quantum simulation methods employ empirical correction schemes on top of classical simulations to better fit a particular macro/microscopic observable. This can lead optimized pair potentials to severely over fit to one particular thermodynamic state.³ This has lead researchers to pursue simulation methods that can better represent the physics of the liquid state without the need for empirical correction. A rigorous way of doing this is through the use of quantum mechanics and the path integral.⁴ The aim of this review is to convince newcomers of the power of path integral simulations as well as reveal the often overlooked theoretical background of quantum simulation.

I. INTRODUCTION

The history of path integrals starts with a small comment in Dirac's notes about how the probability amplitude can correspond to the classical action.⁵ Richard Feynman saw this and was able to flesh out the details and entirely reformulate quantum mechanics. A proof of the equivalence between the Feynman approach and the historical one can be shown by taking the probability amplitude of a particle $\langle x', t | x_0, t_0 \rangle = \langle x', t_0 | U(t) | x_0, t_0 \rangle$ and then splitting the time evolution operator between them into P parts.⁵ Contemporaneously to Feynman's derivation of the path integral there was a revolution within the world of liquid state physics. Nicholas Metropolis had taken the first steps towards simulation the microscopic physics of liquids on computers.⁶ With his invention of the Metropolis Monte Carlo algorithm, it became possible to observe the exact motions of particles which obey the rules of the Lennard-Jones pair potential. Via the ergodic theory of Von Neumann it became possible to reformulate these Monte Carlo simulations through the lens of dynamics rather than the inherent probabilistic methods.⁷ The culmination of computational and theoretical development birthed a new field of study. Researchers in the fields of physics, biology, and chemistry ran classical molecular dynamic simulations to observe the effects of simulation parameters on PV diagrams, heat capacity, pair correlation functions, diffusion coefficients, etc.²

A growing concern within these fields that the pair potentials found by empirical algorithmic methods lack transferability as well as ability to effectively approximate third body effects.³ The inexactness of empirical corrections combined with a clear lack of uncertainty quantification of these classical algorithms has ushered researchers to fall back on *ab initio* techniques.⁸ An obvious method that should give minimal error with respect to experimental results is solving the time-dependent Schrödinger equation for the nuclei and electrons simultaneously. However, this method fails to be computationally feasible for non-trivial systems. Any system involving more than three particles requires an iterative solution. When considering the usual particle count in MD simulations being on the order of 1000 or higher, *ab initio* tech-

niques within the Schrödinger picture of quantum mechanics seemed out of reach. At this point researchers took Feynman's advice "Any good theoretical physicist knows 6 or 7 theoretical representations for exactly the same physics, and he keeps them in his head to hopefully give him different ideas for guessing".⁹ Rather than caring about the exact dynamics of a many body system, researchers utilized the power of the statistical ensemble similarly to the original ideas of Metropolis that founded liquid simulation. It has long been known that evaluating the probability amplitude of a particle that starts and ends in the same position at an imaginary time recovers the elements of the statistical ensemble operator $\rho(x_0, x_0; \beta)$. More precisely $\langle x_0, t_0 | U(t) | x_0, t_0 \rangle$ evaluated at $t = -i\tau$ such that $\tau = \beta\hbar$ is equal to $\rho(x_0, x_0; \beta)$.¹⁰ This equivalence was the clue scientists needed to rewrite $\rho(x_0, x_0; \beta)$ in it's path integral form similarly to the probability amplitude $\langle x_0, t_0 | U(t) | x_0, t_0 \rangle$. In doing this, researchers performed exactly the same feat as Feynman and totally reformulated quantum statistical mechanics as well as quantum simulation.¹¹

Often the details of the path integral formalism are overlooked when learning quantum or statistical mechanics; in fact, most universities lack a course on quantum simulations of liquids despite their growing importance in a broad range of scientific disciplines. Hence, there is a clear need for an educational document that outlines the theoretical and numerical implementation of path integral molecular dynamics. One such detail that is specifically addressed in this paper is the trotter factorization, which is foundational to the theory of path integrals since the rules of scalars and finite systems cannot be applied when dealing with infinite dimensional operators.¹² This review includes a detailed derivation of the isomorphism between the path integral formalism and a classical system of ring polymers as well as provides resources to run path integral simulations.

II. THEORETICAL DERIVATION

When it comes to statistical mechanics, the partition function is everything. It allows a connection between micro-

scopic statistical mechanics and the macroscopic thermodynamic measurements. Consider how the average energy relates to the partition function $\langle E \rangle = -\frac{\partial Q}{\partial \beta}$.¹³ Multiplying the average energy by the number of particles gives the internal energy function. Taking particular derivatives of this function will result in any possible thermodynamic observable. This implies an important corollary: if two systems share a partition function, they are equivalent in a thermodynamic sense. Considering this fact in tandem with the seemingly mystical connection between the partition function and the propagator, lets observe the consequences of writing the partition function as a path integral. Exploring this aspect within the propagator can give a whole new view on quantum mechanics; similarly, one can gain new insight into quantum statistical mechanics in the same manner.

To start, consider the quantum mechanical partition function for a single particle in an NVT ensemble.¹³ The particle is located within a box of length L with periodic boundary conditions. This choice of boundary conditions is the most common choice for both simulation and condensed matter physics problems. Periodic boundary conditions allow the results to better represent macroscopic systems sizes without actually having a large simulation.

$$Q_{1VT} = \text{Tr}(\exp(-\beta\mathbf{H})) \quad (1)$$

The trace of an operator can be written in any basis.¹⁰ Strategically write Q in terms of the position basis $\{\mathbf{r}\}$.

$$\text{Tr}(\exp(-\beta\mathbf{H})) = \int d\mathbf{r} \langle \mathbf{r} | \exp(-\beta\mathbf{H}) | \mathbf{r} \rangle \quad (2)$$

Where the integration is over all co-ordinates of space. Such as x, y, z in Cartesian or r, θ, ϕ in spherical. Consider just the operator within the integral. Performing a trotter factorization similarly to the regular path integral results in the following quantity:

$$\exp(-\beta\mathbf{H}) \approx \exp(-\beta\mathbf{H}/P)^P \quad (3)$$

Where the approximation becomes an equality in the limit $\lim_{P \rightarrow \infty}$. Note that this formula is presented without mathematical proof. A proof of this theorem can be seen in Trotters original paper from 1959, or within the texts from Schulman in 1981, and from Tuckerman in 2010.^{12,14,15} Putting this factorization within the trace operation results in:

$$\int d\mathbf{r} \langle \mathbf{r} | \exp(-\beta\mathbf{H}/P)^P | \mathbf{r} \rangle \quad (4)$$

Consider the identity written in the position basis:

$$\mathbf{1} = \int d\mathbf{r} |\mathbf{r}\rangle \langle \mathbf{r}| \quad (5)$$

Inserting this identity between each of the terms being multiplied results in:

$$\int d\mathbf{r}^1 \int d\mathbf{r}^2 \dots \int d\mathbf{r}^P \langle \mathbf{r}^1 | \exp(-\beta\mathbf{H}/P) | \mathbf{r}^2 \rangle \dots \langle \mathbf{r}^P | \exp(-\beta\mathbf{H}/P) | \mathbf{r}^1 \rangle \quad (6)$$

Notice that each term being multiplied is simply a term within the density matrix $\rho(\mathbf{r}_a, \mathbf{r}_b; \beta/P)$ where the temperature has been raised by a factor of P .² Expanding one of the terms Hamiltonian in terms of the potential energy and kinetic energy contributions gives:

$$\rho(\mathbf{r}^a, \mathbf{r}^b; \beta/P) = \langle \mathbf{r}^a | \exp(-\beta\mathbf{H}/P) | \mathbf{r}^b \rangle \quad (7)$$

$$= \langle \mathbf{r}^a | \exp(-\beta(\mathbf{T} + \mathbf{V})/P) | \mathbf{r}^b \rangle \quad (8)$$

$$= \langle \mathbf{r}^a | \exp(-\beta(\mathbf{T}/P) \exp(-\beta\mathbf{V}/P) | \mathbf{r}^b \rangle \quad (9)$$

By inserting the identity between the two exponentials we can simplify the expression further. Then via the eigenvalue eigenvector relation between the potential energy and the position basis we can extract one of the terms.

$$= \int d\mathbf{r}_c \langle \mathbf{r}^a | \exp(-\beta(\mathbf{T}/P) | \mathbf{r}^c \rangle \langle \mathbf{r}^c | \exp(-\beta\mathbf{V}/P) | \mathbf{r}^b \rangle \quad (10)$$

$$= \exp(-\beta\mathbf{V}(\mathbf{r}^b)/P) \int d\mathbf{r}_c \langle \mathbf{r}^a | \exp(-\beta(\mathbf{T}/P) | \mathbf{r}^c \rangle \langle \mathbf{r}^c | \mathbf{r}^b \rangle \quad (11)$$

$$\implies \rho(\mathbf{r}^a, \mathbf{r}^b; \beta/P) = \langle \mathbf{r}^a | \exp(-\beta\mathbf{T}/P) | \mathbf{r}^b \rangle \exp(-\beta\mathbf{V}(\mathbf{r}^b)/P) \quad (12)$$

Because we are taking the limit that $P \rightarrow \infty$ this is a true equality and not an approximation.¹² The kinetic energy term just corresponds to the non normalized free particle density matrix at a temperature multiplied by a factor of P .

$$\langle \mathbf{r}^a | \exp(-\beta\mathbf{T}/P) | \mathbf{r}^b \rangle \propto \rho_{\text{free}}(\mathbf{r}^a, \mathbf{r}^b; \beta/P) \quad (13)$$

In order to continue we have to calculate the free particle density matrix. This is most easily done by inserting the momentum space identity.

$$\langle \mathbf{r}^a | \exp(-\beta\mathbf{T}/P) | \mathbf{r}^b \rangle = \sum_{\mathbf{k}} \langle \mathbf{r}^a | \exp(-\beta\mathbf{T}/P) | \mathbf{k} \rangle \langle \mathbf{k} | \mathbf{r}^b \rangle \quad (14)$$

$$= \sum_{\mathbf{k}} \langle \mathbf{r}^a | \mathbf{k} \rangle \langle \mathbf{k} | \mathbf{r}^b \rangle \exp\left(-\frac{\beta\hbar^2\mathbf{k}^2}{2Pm}\right) \quad (15)$$

$$= \left(\frac{1}{2\pi}\right)^3 \sum_{\mathbf{k}} \exp(i\mathbf{k}(\mathbf{r}^a - \mathbf{r}^b)) \exp\left(-\frac{\beta\hbar^2\mathbf{k}^2}{2Pm}\right) \quad (16)$$

At this point we can approximate the summation using an integral. The summation is used within this problem simply because there is a countable set of allowed \mathbf{k} space values.¹⁶ This implies a \mathbf{k} space density. Multiplying by the \mathbf{k} space density over itself produces an equivalent expression.

$$\sum_{\mathbf{k}} F(\mathbf{k}) = \frac{1}{\Delta\mathbf{k}} \sum_{\mathbf{k}} F(\mathbf{k}) \Delta\mathbf{k} \quad (17)$$

The density of \mathbf{k} space values is simply 1 allowed \mathbf{k} value every $(\frac{2\pi}{L})^3 = (\frac{8\pi^3}{V})$. Taking the limit as the system size increases makes $\Delta\mathbf{k}$ approach an infinitesimal $d\mathbf{k}$.¹⁶

$$\sum_{\mathbf{k}} F(\mathbf{k}) \approx \left(\frac{V}{8\pi^3}\right) \int d\mathbf{k} F(\mathbf{k}) \quad (18)$$

Replacing the actual function for $F(\mathbf{k})$ gives:

$$\begin{aligned} & \left(\frac{1}{2\pi}\right)^3 \sum_{\mathbf{k}} \exp(i\mathbf{k}(\mathbf{r}^a - \mathbf{r}^b)) \exp\left(-\frac{\beta\hbar^2\mathbf{k}^2}{2Pm}\right) \quad (19) \\ &= \left(\frac{1}{2\pi}\right)^3 \left(\frac{V}{8\pi^3}\right) \int d\mathbf{k} \exp(i\mathbf{k}(\mathbf{r}^a - \mathbf{r}^b)) \exp\left(-\frac{\beta\hbar^2\mathbf{k}^2}{2Pm}\right) \quad (20) \end{aligned}$$

The \mathbf{k} vector is a quantity that contains the set of three values $\{k_x, k_y, k_z\}$. Utilizing this we can easily rewrite the expression in terms of a summation over x, y, and z. A summation inside an exponential will result in a product outside.

$$= \int \prod_{j=x,y,z} dk_j \exp\left(ik_j(\mathbf{r}_j^a - \mathbf{r}_j^b) - \frac{\beta\hbar^2 k_j^2}{2Pm}\right) \quad (21)$$

All directions will integrate to the same value due to \mathbf{k} space being isotropic. So we can just cube the integral of one dimensions. Resulting in the final expression:

$$= \left(\frac{1}{2\pi}\right)^3 \left(\frac{8\pi^3}{V}\right) \left(\int dk_x \exp\left(ik_x(\mathbf{r}_x^a - \mathbf{r}_x^b) - \frac{\beta\hbar^2 k_x^2}{2Pm}\right)\right)^3 \quad (22)$$

We can complete the square within the exponential to make the integral more obvious. Choose $B = \frac{\beta\hbar^2}{Pm}$ as well as $k_0 = i(\mathbf{r}_x^a - \mathbf{r}_x^b)/B$. This implies the integral can be reduced to:

$$\implies = \int dx \exp\left(-\frac{B}{2}\left(-2k_0 k_x + k_x^2 + k_0^2 - k_0^2\right)\right) \quad (23)$$

$$= \int dk_x \exp\left(-\frac{B}{2}\left((k - k_0)^2 - k_0^2\right)\right) \quad (24)$$

$$= \exp\left(\frac{Bk_0^2}{2}\right) \int dk_x \exp\left(-\frac{B}{2}(k - k_0)^2\right) \quad (25)$$

$$= \exp\left(\frac{Bk_0^2}{2}\right) \sqrt{\frac{2\pi}{B}} \quad (26)$$

Plugging this back into the original expression yields the following:

$$= \frac{V}{8\pi^3} \frac{1}{8\pi^3} \left(\frac{2\pi}{B}\right)^{3/2} \exp\left(\frac{3Bk_0^2}{2}\right) \quad (27)$$

$$= \frac{V}{8\pi^3} \left(\frac{Pm}{2\pi\beta\hbar^2}\right)^{3/2} \exp\left(-\frac{Pm(\mathbf{r}^a - \mathbf{r}^b)^2}{2\beta\hbar^2}\right) \quad (28)$$

Notice the term exponentiated to the 3/2 in the prefactor. It is exactly the same as an integrated quasi-classical momentum distribution.

$$Q_{Free} = \int d\mathbf{p} \frac{1}{8\pi^3\hbar^3} \exp\left(-\frac{\beta\mathbf{p}^2}{2Pm}\right) = \left(\frac{Pm}{2\pi\beta\hbar^2}\right)^{3/2} \quad (29)$$

This implies that the element of $\langle \mathbf{r}^a | T/P | \mathbf{r}^b \rangle$ is proportional to:

$$\begin{aligned} & \langle \mathbf{r}^a | \exp(-\beta\mathbf{T}/P) | \mathbf{r}^b \rangle \quad (30) \\ & \propto \left(\frac{Pm}{2\pi\beta\hbar^2}\right)^{3/2} \exp\left(-\frac{Pm(\mathbf{r}^a - \mathbf{r}^b)^2}{2\beta\hbar^2}\right) = Q_{Free} Q_{Harmonic} \quad (31) \end{aligned}$$

Combining this with the potential energy portion within the full partition function gives:

$$\begin{aligned} Q_{1VT} &= Q_{RP} \quad (32) \\ &= \prod_{i=1}^P \int d\mathbf{r}^i \left(\frac{Pm}{2\pi\beta\hbar^2}\right)^{3/2} \exp\left(-\frac{Pm(\mathbf{r}^i - \mathbf{r}^{i+1})^2}{2\beta\hbar^2}\right) \exp(-\beta\mathbf{V}(\mathbf{r}^i)/P) \quad (33) \end{aligned}$$

This is simply the partition function for a ring polymer with P beads. The potential energy function acts exactly the same as a classical one. It takes in just the co-ordinates of one bead at a time as indicated by the superscript on the \mathbf{r} . This means that the beads with different labels do not interact via the classical potential. Expanding this one particle partition function into an N particle partition function generally follows a similar process. The only extra work involved is ensuring that indistinguishability is accounted for. The N particle one looks like the following:²

$$\begin{aligned} Q_{NVT} &= \frac{1}{(NP)!} \left(\frac{Pm}{2\pi\beta\hbar^2}\right)^{3NP/2} \quad (34) \\ &\times \prod_{n=1}^N \prod_{i=1}^P \int d\mathbf{R}_n^i \exp\left(-\frac{Pm(\mathbf{R}_n^i - \mathbf{R}_n^{i+1})^2}{2\beta\hbar^2}\right) \exp(-\beta\mathbf{V}(\mathbf{R}_n^i)/P) \quad (35) \end{aligned}$$

A diagrammatic interpretation of the interactions between particles is shown in figure 1.

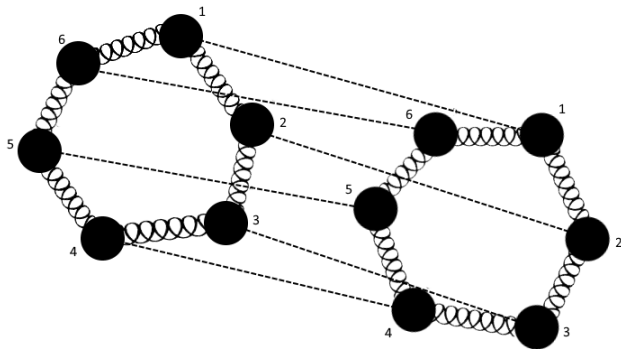


FIG. 1. A system of 2 molecules split into 6 subsystems. Notice the springlike interaction between beads of different labels and the regular potential energy interaction between those of the same label.

Thus we have shown that the partition function for a system of ring polymers is mathematically equivalent to that of a quantum mechanical system of particles. Therefore, by simulating a liquid ensemble of ring polymers with a particular potential energy function, we can achieve a simulated quantum mechanical system of particles. When calculating thermodynamic observables, just average over the P systems being simultaneously simulated.

III. IMPLEMENTATION

Rather than utilize this paper to explain each line of code required to run a path integral simulation, this section will outline the main places and packages to learn this aspect. Creation of an entire simulation package from scratch is tedious and unimportant for simple application of the tool. The industry standard is to make modifications of a few key tools rather than personalized code.

The most commonly used tool for numerical PIMD simulations is the combination of I-Pi: A universal force engine with LAMMPS (Large-scale Atomic/Molecular Massively Parallel Simulator).^{17,18} I-Pi is an easy to use python interface that is designed to interact with LAMMPS and other *ab initio* force field calculators efficiently and effectively. I-Pi acts on a server client basis. Such that I-Pi acts as a manager of nuclei positions and outsources the force calculation to its employee LAMMPS. While there is no formal textbook or paper that outlines the exact details of running a simulation with I-Pi, there is a very good series of Jupyter notebooks that outline the installation and python used to run I-Pi simulations. The tutorials can be found on I-Pi's GitHub page.¹⁹ Specifically, these tutorials go over how to install I-Pi, LAMMPS and CP2K. Details on running simulations of water and other materials are provided as well.

In order to verify that the reader fully understands how to utilize this software, I recommend attempting to simulate something that is not within the tutorial files directly. For

example, creating an original LAMMPS data file containing 216 water molecules. Then utilizing the TIP4P potential energy function provided within day 2 of the tutorial.²⁰ Then running multiple simulations at differing bead counts observing the effect on the bond angle and bond length of the water molecules. For comparison, the results of my execution of this exercise are shown in figures 2 and 3.

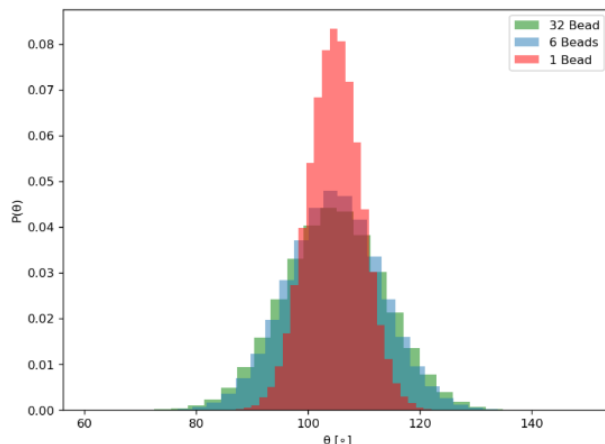


FIG. 2. A distribution of observed bond angles in an NVT simulation of water molecules. $T = 300$ K, Box Length = 36 \AA , $N = 216$

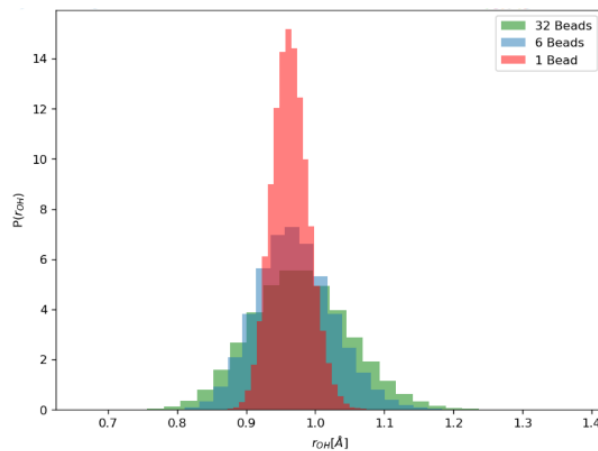


FIG. 3. A distribution of observed bond distances in an NVT simulation of water molecules. $T = 300$ K, Box Length = 36 \AA , $N = 216$

IV. FURTHER RESEARCH

While the implementation of PIMD presented here does accurately predict the behavior of some materials from the atomic to macroscopic scale, it does not tell the entire story of quantum mechanics. Thus, it remains to show the details of electronic structure calculation and direct implementation of the fundamental properties of bosons and fermions. Further research on implementation of bosonic mechanics can be found in the paper by Hirshberg, Rizzi, and (as usual)

Parrinello.²¹ Briefly, they show that through a recursive algorithm that doesn't explore all bosonic permutations, they can effectively model thermodynamic averages present in bosonic systems. Their results have been shown to approximate 2D systems with only an $O(N^3)$ penalty W.R.T the number of particles. Verification of these results has been shown by comparison to numerical diagonalization of the many body Hamiltonian. For inclusion of electronic structure calculation see the work done by the Quantum Espresso group.²² The inclusion of Quantum Espresso with I-Pi's quantum nuclear effects is quite simple, however the theoretical background is quite complicated. Quantum Espresso is just one tool of many, and the field of electronic structure calculation is growing with the development of density function theory. A proper description of this aspect of PIMD would take numerous publications and deserves its own review.

PIMD is not restricted to generic calculations of gaseous and liquid state thermodynamic properties. In 2018 Ramirez and Herrero were able to combine the electronic structure tight binding Hamiltonian and PIMD quantum nuclear effects within one simulation scheme.²³ Their results had good agreement with spectroscopic ellipsometry and with perturbative theoretical results. PIMD has also been a key player in the verification of the isotopologue assumption commonly used within structure potential refinement schemes. A qualitative verification of PIMD's effects on structure can be seen in the bonding distribution plots shown in figures 2 and 3. A decisive experimental and computational study into the isotope effects on water's structure was done in 2012 by Zeidler and others.²⁴ They were able to verify that both deuterated and hydrogenated water both gave the same structure results, which was only possible through the use of PIMD. Thereby solidifying PIMD's position as a tool for scientific discovery.

Lastly, there is a clear need to mitigate the prohibitive time complexity bounds in path integral molecular dynamics. There is an innate and unavoidable $O(P)$ increase in time complexity when simulating P replicates of the original system.² It can require up to 24 hours of computation on highly parallel machines to simulate a systems of organic molecules classically. If researchers ever hope to get the same results with a PIMD solution they will be heavily hindered by the $O(P)$ growth. It is also clear that purely empirical corrections of classical simulations are dependent on the thermodynamic state to which they were optimized.^{3,25} Therefore, there is an urgent need to find theoretical quantum coarse graining solutions. Recently, Scott Shell has released a landmark paper on multi-scale modeling, in which he utilized the relative entropy between two phase space distributions to quantify coarse grained molecular potentials.²⁶ Going from atoms to molecules is quite similar to the transition from a quantum particle to a classical one, this implies the existence of a algorithm to transition between quantum potential energy functions and their approximate classical counterparts. If implemented successfully, PIMD simulations may be able to be run with only an $O(1)$ increase in complexity compared to classical ones.

V. CONCLUSIONS

This study has outlined the key aspects of deriving the path integral representation of molecular dynamics. By splitting the Hamiltonian into P pieces and utilizing several eigenvector-eigenvalue relations, one can prove the partition function of a system of ring polymers is isomorphic to the quantum partition function.^{24,11} The ability to model quantum nuclear effects in systems of many particles has lead to PIMD's widespread adoption in biology, chemistry, and physics. Each of these fields has been able to tailor the simulations to exactly their needs. For example, the physics scientific community has successfully extended PIMD to systems of bosonic fluids, fermionic fluids, and crystalline solids.²¹

However, PIMD is far from a perfect tool. The time complexity is limiting for researchers studying complex systems at macroscopic length and time scales⁸. Thus, there is an urgent need to develop theoretically backed methods that can perform accurate quantum simulations with an $O(1)$ complexity penalty. Lastly, the mystical nature of this approximation has yet to be explained. The underlying model connections between classical and quantum statistical mechanics are numerous and should not be limited to PIMD. By exploiting these connections, scientists may discover new perspectives on modern physics.

REFERENCES

- ¹J. G. Kirkwood and F. P. Buff, "The statistical mechanical theory of solutions. i," **19**, 774–777, [_eprint: https://doi.org/10.1063/1.1748352](https://doi.org/10.1063/1.1748352).
- ²M. P. Allen and D. J. Tildesley, *Computer Simulation of Liquids: Second Edition: 9780198803201*.
- ³A. Louis, "Beware of density dependent pair potentials," **14**, 10.1088/0953-8984/14/40/311.
- ⁴D. Marx and M. Parrinello, "Ab initio path integral molecular dynamics: Basic ideas," **104**, 4077, publisher: American Institute of PhysicsAIP.
- ⁵R. P. Feynman, *QED: The Strange Theory of Light and Matter (Princeton Science Library, 33)*.
- ⁶N. Metropolis, A. W. Rosenbluth, M. N. Rosenbluth, A. H. Teller, and E. Teller, "Equation of state calculations by fast computing machines," **21**, 1087–1092, [_eprint: https://doi.org/10.1063/1.1699114](https://doi.org/10.1063/1.1699114).
- ⁷J. v. Neumann, "Proof of the ergodic theorem and the h-theorem in quantum mechanics," **35**, 201–237, publisher: Springer Science and Business Media LLC.
- ⁸P. Faccioli, M. Sega, F. Pederiva, and H. Orland, "Dominant pathways in protein folding," *Phys. Rev. Lett.* **97**, 108101 (2006).
- ⁹F. Street, "Richard feynman teaches you the scientific method," .
- ¹⁰R. Shankar, *Principles of Quantum Mechanics, 2nd Edition: Shankar, R.*
- ¹¹D. Chandler and P. G. Wolynes, "Exploiting the isomorphism between quantum theory and classical statistical mechanics of polyatomic fluids," **74**, 4078, publisher: American Institute of PhysicsAIP.
- ¹²H. F. Trotter, "On the product of semi-groups of operators," **10**, 545–551.
- ¹³I. Kusaka, *Statistical Mechanics for Engineers* (Springer International Publishing, 2015).
- ¹⁴L. Schulman, *Techniques and Applications of Path Integration* (Wiley).
- ¹⁵M. Tuckerman, *Statistical Mechanics: Theory and Molecular Simulation* (OUP Oxford).
- ¹⁶N. Ashcroft and N. D. Mermin, *Solid State Physics* (Cengage Learning).
- ¹⁷M. Ceriotti, J. More, and D. E. Manolopoulos, "i-PI: A python interface for ab initio path integral molecular dynamics simulations," **185**, 1019–1026.
- ¹⁸A. P. Thompson, H. M. Aktulga, R. Berger, D. S. Bolintineanu, W. M. Brown, P. S. Crozier, P. J. in 't Veld, A. Kohlmeyer, S. G. Moore, T. D.

- Nguyen, R. Shan, M. J. Stevens, J. Tranchida, C. Trott, and S. J. Plimpton, "LAMMPS - a flexible simulation tool for particle-based materials modeling at the atomic, meso, and continuum scales," **271**, 108171.
- ¹⁹V. Kamil, E. Pos, and M. Rossi, "I-pi/tutorials-schools," (2021).
- ²⁰J. L. F. Abascal and C. Vega, "A general purpose model for the condensed phases of water: Tip4p/2005," *The Journal of Chemical Physics* **123**, 234505 (2005), <https://doi.org/10.1063/1.2121687>.
- ²¹B. Hirshberg, V. Rizzi, and M. Parrinello, "Path integral molecular dynamics for bosons," *Proceedings of the National Academy of Sciences* **116**, 21445–21449 (2019).
- ²²P. Giannozzi, S. Baroni, N. Bonini, M. Calandra, R. Car, C. Cavazzoni, D. Ceresoli, G. L. Chiarotti, M. Cococcioni, I. Dabo, A. D. Corso, S. de Gironcoli, S. Fabris, G. Fratesi, R. Gebauer, U. Gerstmann, C. Gougoussis, A. Kokalj, M. Lazzeri, L. Martin-Samos, N. Marzari, F. Mauri, R. Mazzarello, S. Paolini, A. Pasquarello, L. Paulatto, C. Sbraccia, S. Scandolo, G. Sclauzero, A. P. Seitsonen, A. Smogunov, P. Umari, and R. M. Wentzcovitch, "Quantum espresso: a modular and open-source software project for quantum simulations of materials," *Journal of Physics: Condensed Matter* **21**, 395502 (2009).
- ²³R. Ramírez, C. P. Herrero, and E. R. Hernández, "Path-integral molecular dynamics simulation of diamond," **73**, 245202, publisher: American Physical Society.
- ²⁴A. Zeidler, P. S. Salmon, H. E. Fischer, J. C. Neufeind, J. M. Simonson, and T. E. Markland, "Isotope effects in water as investigated by neutron diffraction and path integral molecular dynamics," **24**, 284126, publisher: IOP Publishing.
- ²⁵B. L. Shanks, J. J. Potoff, and M. P. Hoefner, "Transferable force fields from experimental scattering data with machine learning assisted structure refinement," *The Journal of Physical Chemistry Letters* **13**, 11512–11520 (2022).
- ²⁶M. S. Shell, "The relative entropy is fundamental to multiscale and inverse thermodynamic problems," *The Journal of Chemical Physics* **129**, 144108 (2008), <https://doi.org/10.1063/1.2992060>.