Solution to partition function for macroscopic condensed matters – the key problem of statistical physics

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The key problem of statistical physics standing over one hundred years is how to exactly calculate the partition function of macroscopic condensed matters, which severely hinders application of the theory to predict many properties of realistic systems. Here we present a novel approach which works at least four orders faster than ab-initio algorithms to the problem and can be applied to predict thermal properties of macroscopic condensed matters via ab initio calculations. The method was demonstrated by solid and liquid Copper (up to 2500K and ~600GPa), and the derived internal energy and pressure are in a good agreement with the results of vast molecular dynamics simulations, achieving a precision at least one order higher than previous methods. And, for the first time, the realistic isochoric equation of state for solid argon was reproduced directly from the partition function.

By the end of 19th century, the born of statistical physics brought a promising prospect that all the thermodynamic properties of macroscopic systems, such as equation of states (EOSs) [1, 2], the conditions for phase transitions (i.e., phase diagrams) [3], can be thoroughly predicted without empirical data by calculating the partition function (PF). Nevertheless, it was soon realized that such an implementation is impossible for condensed matters [4] because PF is in principle determined by all the possible microstates over entire phase space and we have to deal with a 3N-fold integral to obtain the PF for a system consisting of N particles, which goes far beyond the capability of modern supercomputers if the standard algorithm of numerical integral is applied [5]. For instance, a rough calculation of PF for a C60 molecule, involving a 180-fold integral, would cost at least 10^100 years by using even the fastest high-performance computing facility with ~10^16 FP64 operations per second.

Alternative routes are resorted to sampling approaches, that is, either following the formalism of molecular dynamics (MD) simulation to trace the trajectories by integrating Newton’s equation of motion [6], or, in a manner of Monte Carlo (MC) way to visit the microstates with substantial contributions to PF by stochastic walk in phase space [7]. Although time-average-based MD and ensemble-average-based MC algorithms have been developed over half a century and proved to be impressive to gain mechanical properties [8], when it comes to thermodynamic properties, the long-standing problem in face of both schemes remains that a balance has to be reluctantly sought for between limited-length sampling and the demanding requirement of ergodicity as the size of a system increases [9]. Progress has been made in evaluations of the relative difference of PF (or free energy) [10, 11], and more attentions are being paid to the density of state to calculate absolute PF [12, 13]. Nested sampling may be state-of-the-art technique [17], which aims at uniformly sampling a series of fixed fractions partitioned by potential energies in configurational space [18, 19] and has been successfully applied in several aspects [20–30]. Despite of the improved 2-3 orders of efficiency, the method may also suffer from the broken ergodicity [31] and the affordable size of systems is still limited on the scale of 10^2 particles. Especially, the large computational cost yet prohibits ab initio calculations readily implemented in the algorithm.

In this work, instead of tackling PF in the fashion of sampling, we established a direct integral approach (DIA) to solve the 3N-fold integral on the basis of reinterpretation of original sense of integral, the ultrafast speed of which makes it possible that calculations of PF for condensed systems consisting of more than 10^5 particles can be achieved on a desktop personal computer. Validations of the method were made in Copper and Argon systems, where EOSs of solid and liquid Copper obtained by DIA were compared with MD simulations using same empirical potentials, and for solid Argon, the computed isochoric EOS under high pressure zone were directly compared with experiments. Excellent agreements confirmed the accuracy of DIA. Ultrahigh efficiency of DIA paves a way to calculate the PF of macroscopic condensed matters with ab initio computations.

DIRECT INTEGRAL APPROACH TO PARTITION FUNCTION: REINTERPRETATION OF INTEGRAL

The original sense of one-fold (1D) integral \( I_{1D} = \int_a^b f(x)dx \) is interpreted as the sum of infinite number of rectangles with area \( A_i = f(x_i)\Delta x \), and \( I_{1D} = \lim_{\Delta x \to 0} \sum A_i \). Here, we interpret the integral from a different angle: The length of the 1D element \( \Delta x \) at
x_i is modulated by f(x_i) to be a new length element \( \Delta x_i' = \int f(x_i) dx \) and \( I_{1D} = \sum_i \Delta x_i' \). In other words, 1D integral is mapped to a summation of length elements instead of area elements and equals to an effective length of \( b-a \) (see top panel in Fig.1). Similarly, a two-fold integral \( I_{2D} = \int f(x,y)dxdy \) equals to an effective area of \( a \cdot b \) because the area element \( ds = dx dy \) is enlarged (or shrunk) by \( f(x,y) \) giving rise to an effective area element \( ds' = \int f(x,y)dxdy \) (see bottom panel in Fig.1). Followed by this notion, an \( N \)-fold integral \( I_{ND} = \int \int \ldots \int d\mathbf{q}_1 d\mathbf{q}_2 \ldots d\mathbf{q}_N f(q_1,q_2 \ldots q_N) \) equals to an effective volume of \( a_1 \cdot a_2 \ldots a_N. \)

When the integrand \( f(q_1,q_2 \ldots q_N) \) is in a form of \( \exp[-U(q_1,q_2 \ldots q_N)] \) with \( U(q_1,q_2 \ldots q_N) \) being positive definite within the entire integral domain and having minimum at the origin \( U(0) = 0 \), the effective length of \( a_i \) is defined as

\[
a_i' = \int_0^{a_i} \exp[-U(0 \ldots q_i \ldots 0)]dq_i, \quad (i = 1,2 \ldots N)
\]

and the effective volume approximates to a product \( \prod_{i=1}^{N} a_i' \) (see proof in Supplementary Information), i.e.,

\[
I_{ND} \approx \prod_{i=1}^{N} a_i'.
\]

Now consider the configurational integral (CI) in PF for a continuum system consisting of \( N \) particles at a given temperature \( T \) (see details in Supplementary Information),

\[
Q = \int dq^{3N} \exp[-\beta U(q^{3N})],
\]

where \( \beta = 1/k_BT \) with \( k_B \) the Boltzmann constant, \( q^{3N} = \{ q_1,q_2 \ldots q_N \} \) the Cartesian coordinates of particles and \( U(q^{3N}) \) the potential function. Although the integrand is of the same form as required by equation (2), it may not be positive definite or have no minimum at the origin \( U^{3N}(0) = 0 \). Letting the set \( Q^{3N} = \{ Q_1, Q_2 \ldots Q_{3N} \} \) be the coordinates of particles in state of the lowest potential energy \( U_0 \), we may introduce a function

\[
U'(q^{3N}) = U(q^{3N}) - U_0,
\]

where \( q_i' = q_i - Q_i \). By inserting equation (4) into equation (3), we obtain

\[
Q = e^{-\beta U_0} \int dq^{3N} \exp[-\beta U'(q^{3N})].
\]

Clearly, \( U'(q^{3N}) \) is positive definite within all the integral domain and has minimum at the origin \( U'(0) = 0 \). According to equation (2), the integral in equation (5) equals to an effective 3N-fold volume, so,

\[
Q = e^{-\beta U_0} \prod_{i=1}^{3N} L_i',
\]

where the effective length \( L_i' \) on the \( i \)-th degree of freedom is defined as

\[
L_i' = \int e^{-\beta U'(0 \ldots q_i' \ldots 0)} dq_i'.
\]

In this way, the 3N-fold integral is turned into one-fold integrals.

For some homogeneous systems with certain geometric symmetry, such as perfect one-component crystals, all the particles are equivalent and \( U' \) felt by one particle moving along \( q_i' \) may be the same as the one along \( q_j' \) (or \( q_k' \)). In such a case, equation (5) turns into

\[
Q = e^{-\beta U_0} L'^{3N},
\]

where \( L' \) is the effective length determined by equation (7). Otherwise, it is needed to calculate the effective length, \( L_x', L_y', L_z' \) by equation (7) of an arbitrary particle, and equation (6) turns into

\[
Q = e^{-\beta U_0} (L_x'L_y'L_z')^N.
\]

The procedure can be extended to systems composed of different particle species by calculating the effective length of each species respectively.

For inhomogeneous systems, such as defects or inter-
faces existed, particles may be grouped into $M$ sets numbered by $I$ with each containing $N_I$ equivalent particles, and CI becomes

$$Q = e^{-\beta U_0} \prod_{I=1}^M |V_I'|^{N_I},$$  \hspace{1cm} (10)$$

where $V_I' = \int e^{-\beta U'(x)} dx \int e^{-\beta U'(y)} dy \int e^{-\beta U'(z)} dz$ denotes the effective volume of an arbitrary particle in the $I$th set with Cartesian coordinates $x$, $y$, $z$.

To implement the DIA, the first step is to find the most stable structure (MSS) of the system for determining $U_0$, which can be accomplished in principle by several well-developed methods, such as global optimisations\[32–35\] or dynamic damping\[36, 37\]. Actually, the MSS for crystals can be immediately obtained by placing the particles right at the lattice sites. Then, we move a particle along its one degree of freedom $q_i$ to obtain $U'(0, \ldots, q'_i, \ldots, 0)$ while its other degrees of freedom $q_j$ and all the other particles are kept fixed. Clearly, this is an easy task for ab initio calculations and, therefore, the PF of a $N$-particle system can be obtained even if we have no knowledge about the analytical expression of potential function $U(q^N)$, which is usually hard to be constructed precisely for realistic systems composed of more than one kind of particles.

For testing the DIA, we may perform ab initio calculations of $U'(0, \ldots, q'_i, \ldots, 0)$ on some realistic systems and compare the derived results with related experiments. However, results from first principle calculations may be strongly dependent on different types of exchange-correlation functions and the experimental data are usually insufficient for extensive comparisons. In such cases, even if the results derived from the PF are in good agreement with the experimental data, it would be yet doubted of the accuracy of the DIA. In order to have a stringent test, empirical potentials were used in the computations of PF, and the derived results were compared with the MD simulations using the same potentials to see if there exist some deficiency in the DIA. Considering the large amount of the MD simulations, rather than the calculations of PF by the DIA, we limited the number of atoms in Copper (Cu) system to 4000. For calculating the isochoric EOSs for solid Argon (Ar), by the DIA, 32000 Ar atoms were considered in the system. All the computations based on the DIA were operated on a desktop personal computer with one 3.6GHz AMD Ryzen 7 1800X CPU.

**DIA FOR SOLID AND LIQUID CU**

For the systems of Cu, the interaction between atoms was described by the tight-binding (TB) potential\[38\] and 4000 atoms were confined in a cubic box with periodic boundary condition (PBC) applied. For solid Cu, the MSS was found by arranging the atoms at FCC lattice site. In consideration of the Fm-3m symmetry of FCC lattice, the Cartesian $Z$-axis of atoms is set to [001] direction so that the potential $U'$ felt by an atom moving along the $X$-axis (or $Y$-axis) is the same as the one along the $Z$-axis. To obtain $U'(Z)$, the $Z$ coordinate of the geometry-center atom was changed step by step with its $X$ and $Y$ coordinates fixed to record the potential, during which all the other atoms stay fixed as well. For the liquid system, the atoms were heated up to $2.5 \times 10^4$K in MD simulation to generate a uniform distribution and the damped trajectory method\[36\] was used to determine the MSS and potential energy $U_0$ (see details in Supplementary Information). Different from the cases in crystal Cu, the potential $U'$ felt by a liquid atom moving along the $X$, $Y$, or $Z$-axis may not be the same, so $U'(x)$, $U'(y)$ and $U'(z)$ were calculated respectively and equation (10) was applied to obtain CI.

Common procedures for MD simulations of a canonical ensemble\[37\] was employed to produce the internal energy ($E$) and pressure ($P$) of the systems contacted with a thermal bath at given temperatures, and the Verlet algorithm\[32\] was employed for integrating the equations of motion with time step 0.1 fs and 0.01 fs for solid and liquid respectively. We first fully relaxed the systems for $10^5$ steps, and continued another $10^5$ (or $10^6$) steps to record the values of $E$ and $P$ for solid (or liquid). Atentions have to be paid that the commonly used Virial equations\[9\] are inaccurate to compute pressure in the case of many-body potential with PBC applied\[40, 41\], and we employed the method proposed by Tsai\[42\] that considers stress and momentum flux across an area for conducting the statistic of $P$.

For the solid systems with atomic volume ranging from
Temperature (K)

pressure (RDP=

below 1000K. As shown in Fig.3, the relative difference of

volumes respectively.

FIG. 3. (a) Pressure of solid Cu derived from PF (colored

lines) and MD (colored squares) for different atomic volumes,

(b) relative difference of pressure (RDP) of the two methods,

and (c) relative standard deviation of pressure (RSDP) of MD

simulations. Specific colors correspond to different atomic

volumes respectively.

11.85Å³/atom to 6.07Å³/atom, the internal energy $E_{PF}$

and pressure $P_{PF}$ directly derived from the PF are in ex-

cellent agreement with those ($E_{MD}$ and $P_{MD}$) obtained

by MD simulations at temperatures from 10K to 2500K. As

shown in Fig.2 for $T \leq 1000K$, the relative difference

of internal energy (RDE= $|E_{PF}−E_{MD}|/E_{MD}$) is less

than 0.09% (see data in Supplementary Information). As the

temperature rises up to 2500K, the difference gets a bit larger

(the maximum is 0.69%), which may be attributed to the

statistical fluctuations of MD simulations because the

relative standard deviations of pressure (RSDE), $\sim 0.2\%$, increase by about three times of those ($\sim 0.08\%$)

below 1000K. As shown in Fig.3 the relative difference of

pressure (RDP= $|P_{PF}−P_{MD}|/P_{MD}$) is on the level of $\sim 2\%$
or less, which is larger than RDE. The reason should be that

the MD method for statistic of pressure needs more simu-

lation time since the relative standard deviations of pres-

sure (RSDP), $\sim 10\%$, are about two orders larger than

RSDE. In order to confirm this conjecture, we did similar

comparisons except that the TB potential was replaced

with the Lennard-Jones (L-J) potential[43], for which the

Virial theorem can be applied in the MD simulations to

calculate the pressure exactly. For the volumes of the

system ranging from 11.85Å³/atom to 7.54Å³/atom at

300K, the RSDP reduces down to $\sim 0.03\%$, and corre-

spondingly, the RDP gets smaller to the level of $\sim 0.1\%$.

Figs.2 and 3 show that the internal energy and pressure of

liquid Cu obtained by the DIA are in good agreement with

the MD simulations. The RDE for all the systems is less

than 2%, which is about ten times larger than that for

solid Cu. This difference may stem from the fact that the

$U'(0...q_i,...0)$ felt by a liquid atom differs a little

from that felt by other atoms, which is not the same as the

situation in the solid systems. So, we can perform the

DIA for more liquid atoms to obtain more accurate

results. As to the pressure, the RDP is less than 2% for

most systems except for the one with a density of 8.9

g/cc, which displays larger RDP and can be understood

because the RSDP is apparently larger than other (see

Fig.3).

It should be noted that precision of the DIA is so high

that it has reached limit of the MD simulations. For

instance, the internal energies obtained by the DIA of

solid Cu with the atomic volume of 11.85Å³/atom are

$−13894.76$eV at 300K and $−13383.00$eV at 800K, which

are almost the same as $−13894.96$eV and $−13383.11$eV

obtained by the MD simulations with RSDE of $\sim 0.4\%$. The

trend of RDE and RDP gradually increasing with

temperature should be attributed to the rise of fluctu-

ations of the MD simulation (see Figs.2-3), for which

smaller time step should be applied to integrate the equa-

tions of motion at high temperatures to ensure the pre-

cision.
FIG. 6. Isothermal EOSs of Cu at 298K from the PF using TB[38] (black solid line) and L-J[43] (cyan solid line) potentials for solid Cu are compared with experimental data[44, 45]. The MD simulations with L-J potential are shown in red crosses.

As shown in Fig. 6, the isothermal EOS directly derived from the PF using TB potential[38] exhibits the same trend as the experimental results while the pressures are about 10% larger than the measured values[44, 45]. This discrepancy should be attributed to the inaccuracy of the empirical potential because the pressures obtained by the DIA and MD simulations coincide with each other quite well. By contrast, we also used the L-J potential[43] to calculate the EOS by the DIA. Although the outcome coincides well with the corresponding MD simulations, it deviates much more from the experiments. Accordingly, it calls for a more accurate interatomic potential, which may resort to ab initio calculations in the future.

DIA FOR SOLID AR

To our best knowledge, no accurate EOS has been put forward for solid Ar by directly solving the PF, though various EOSs towards Ar systems have been put forward either based on a fitting-parameter procedure (see detailed reviews in Refs. [46, 47]) or in a MC sampling way for disordered liquid and gas states[24, 48]. Considering that solid Ar has been extensively studied experimentally and is believed to be well characterized by L-J pair potential[5], we calculated the PF of solid Ar by DIA to produce the EOS and compared the results with experiments.

In our work, the system consists of 32000 Argon atoms placed at FCC sites and the computational procedure of DIA was the same as described in the system of solid Cu according to equation(8), except for the interatomic potential being replaced with L-J potential[37]. The isochoric EOSs from PF by DIA and from experiment[49] are shown in Fig. 7 (see data in Supplementary Information). For higher temperature zone where $T \geq 100K$, the maximum relative difference of the pressure between DIA and experiment is around 5%, while the difference gets larger at lower temperatures and the largest one is 13.2% at $T = 80K$, $V = 39.9A^3$/atom ($P_{EXP} = 0.33Kbar$, $P_{DIA} = 0.38Kbar$). According to the original reference[49], uncertainty of the measured pressure at any points ranged from ±50 bars above 80K and becomes larger at lower temperature zone, so we may reach the conclusion that the isochoric EOS derived from DIA is in good agreement with experiment. We want to emphasize again that, because DIA strictly follows the framework of statistical physics, there are no adjustable parameters in our method to determine the EOS and the only possible factor affecting our results may be the appropriateness of the interatomic potential.

FIG. 7. Isochoric EOSs of solid Argon from the PF by DIA (colored lines) and experimental data[49] (colored squares).

CONCLUSION

In summary, by our reinterpretation of integral, DIA to PF of condensed systems was established. The accuracy of DIA was strictly validated by vast MD simulations for condensed Cu and by experiments for solid Ar respectively. As to the efficiency, a comparison made in Supplementary Information demonstrates that the DIA works at least four orders faster than state-of-the-art MC sampling algorithm. The new approach will find its vast applications in investigating the thermodynamic properties of macroscopic systems, which highly relates to designing novel material, predicting various phase transitions and parameter-free EOS under extreme conditions.

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AUTHOR CONTRIBUTIONS

XJN conceived the problem. BYN and XJN co-devised the original idea of DIA. BYN performed the computations of DIA for Cu and Ar systems. BYN and GLC performed the MD simulations using TB and L-J potentials respectively. BYN, TCW and XJN designed and wrote the manuscript together. TCW and XJN co-supervised the work.