PHYSICAL REVIEW E **93**, 063314 (2016)

Extending the parQ transition matrix method to grand canonical ensembles

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(Received 7 December 2015; revised manuscript received 30 May 2016; published 24 June 2016)

Phase coexistence properties as well as other thermodynamic features of fluids can be effectively determined from the grand canonical density of states (DOS). We present an extension of the par$Q$ transition matrix method in combination with the efasTM method as a very fast approach for determining the grand canonical DOS from the transition matrix. The efasTM method minimizes the deviation from detailed balance in the transition matrix using a fast Krylov-based equation solver. The method allows a very effective use of state space transition data obtained by different exploration schemes. An application to a Lennard-Jones system produces phase coexistence properties of the same quality as reference data.

DOI: 10.1103/PhysRevE.93.063314

I. INTRODUCTION

Thermo-physical properties of fluids, and especially their phase transitions, are of great importance not only from a scientific point of view, but also for many engineering applications. Such properties can be obtained by simulating the fluids on a microscopic level by a variety of methods. For known microscopic interactions molecular dynamics as well as Monte Carlo methods are available. In order to obtain reliable data, large enough systems have to be simulated, and even though the increase in computing power has been tremendous, the task of obtaining good predictions for phase change properties is still demanding.

One class of methods to tackle this problem is based on determining the density of states (DOS) for the system under consideration first [1–6]. Then from the obtained DOS the thermophysical equilibrium properties including phase transitions can be deduced in a second step. In order to obtain the DOS a variety of algorithms are available, which can be grouped into histogram- and matrix-based methods. While histogram methods "count" the number of states seen during a random walk through the state space of a system, the matrix methods collect frequencies of potential transitions between states.

The challenge for both classes of algorithms is the fact that for determining phase change properties the DOS needs to be determined not only as a function of the energy but also as a function of the volume (for a fixed particle number) or as a function of the energy and of the particle number present in the system (for fixed volume). This demand for grand canonical DOS or joint DOS (JDOS) increases the numerical effort tremendously, and thus highly efficient algorithms are necessary.

A typical histogram-based method used in this context is the Wang-Laudau algorithm [1,2,7–10], which uses a running estimate of the JDOS to steer a random walker through state space such that the histogram of visits to macrostates becomes flat. Sometimes this approach has the drawback that the recursion used to achieve the flatness may get stuck. Another algorithm which has been used for obtaining JDOS is hyperparallel tempering [11]. A direct approach to observe the phase behavior is through Gibbs ensemble simulations [12–14].

An alternative approach to determine the JDOS is through using transition matrix methods [13,15,16]. Here we present the extension of the par$Q$ method [5,6], a particular transition matrix approach able to collect data from parallel runs, for the task of obtaining the JDOS. An interesting side feature of our approach is the usage of the Wang-Landau algorithm for obtaining the raw data for the transition matrix estimate. The advantage here is that, first, the Wang-Landau algorithm does not need to converge as opposed to its usage in a flat histogram approach, and, second, if it has converged, it can provide a JDOS prediction on its own.

The presentation is organized as follows: first, we give an introduction into the Wang-Landau and the par$Q$ methods, followed by an extension of the par$Q$ method to the grand canonical ensemble. This leads to large sparse transition matrices. Then an efficient method for the computation of the JDOS from sparse transition matrices is presented. Finally we discuss our results for simulations of a Lennard-Jones system and its grand canonical DOS as well as the ensuing phase diagram.

II. EXISTING METHODS FOR DOS AND JDOS DETERMINATION

Histogram- as well as transition matrix-based methods have in common that a base algorithm performs a Monte Carlo walk through the state space of the system. The state space can be either discrete or continuous; for fluids the states are usually described by the (continuous) coordinates of the particles of the system. Each microstate has an energy value assigned to it, here based on the Lennard-Jones interaction potential. The random walk proceeds by selecting a potential neighbor state of the current state as defined by the move class. The proposal probability $q(\omega_c \to \omega_n)$ for a potential transition from the current state ω_c to the neighbor state ω_n characterizes the move class. Whether the proposed neighbor state is accepted or not depends then on the acceptance probability $a(\omega_c \to \omega_n)$, which can be a function, for instance, of the energies of the two states (Metropolis) or of the DOS at the respective energies (Wang-Landau).

In an actual implementation of the algorithms discussed below one needs to set the energy range of interest $[E_{\min}, E_{\max})$ at the start. Then for systems with continuous energies (or huge numbers of discrete states) discretization or lumping of the energy is needed, i.e., all energies in the range

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$[E_i - \frac{\Delta E}{2}, E_i + \frac{\Delta E}{2})$ are lumped into bin i. Based on this lumping the proposal probability $q(\omega_c \to \omega_n)$ on the level of microstates leads to an "infinite temperature" transition matrix Q_{ij}, which reflects the transition frequencies between energy (or macro-) states E_i and E_j if the acceptance probability is set to one: $a(\omega_c \to \omega_n) = 1$.

Below we will focus on two DOS methods employed in this study, one histogram- and one transition matrix-based. These are the Wang-Landau algorithm (WL method) including its extension to determine the JDOS of systems [7,8] and the par$Q$ method with its extension.

A. The Wang-Landau method

The Wang-Landau algorithm is a flat histogram method for Monte Carlo simulations that samples a generalized ensemble. In the standard variant for obtaining the DOS it samples a previously defined energy range $E_{\min} \leqslant E < E_{\max}$ uniformly by accepting proposed moves with the probability

$$a(E_i \to E_j) = \min\left[1, \frac{\Omega(E_i)}{\Omega(E_j)}\right], \tag{1}$$

where E_i and E_j are the energy levels before and after the move. Starting from an initial guess of the DOS $\Omega(E)$ it tries to estimate the exact DOS $\hat{\Omega}(E)$ by modifying $\Omega(E)$ in every Monte Carlo step by $\Omega_{t+1}(E_n) = \Omega_t(E_n) \cdot f$, where $f > 1$ is a modification factor and E_n is the energy after the evaluation of the acceptance criterion. A histogram $H(E)$ is modified simultaneously according to $H_{t+1}(E_n) = H_t(E_n) + 1$. If a move generates a state outside the predefined energy range, it is rejected and $\Omega(E)$ and $H(E)$ are updated at the previous energy [17].

If no initial guess can be made $\Omega(E)$ is set to 1 and $H(E)$ is set to 0 for all E in the range of interest. The modification factor is set to $f_0 = e^1$ at the beginning of the algorithm [1,2]. It is modified according to $f_{k+1} = \sqrt{f_k}$, when a specific flatness condition is met. Here k counts the number of refinements. We finally mention that in an implementation it is advisable to use $\ln \Omega(E_i)$ instead of $\Omega(E_i)$ itself.

Extending the Wang-Landau method to the grand canonical ensemble allows direct access to several observables depending on the chemical potential. To achieve this Shell *et al.* [7] extended the Wang-Landau algorithm to the grand canonical (μVT) and the isothermal-isobaric ensemble (NpT). For the μVT and the NpT ensembles they provided formulas for the acceptance criteria for moves changing either particle number or volume. They present two sets of formulas, one using the configurational DOS Ω and one using the excess DOS Ω_{ex}, where for the latter the ideal gas contribution to the DOS Ω_{ig} has been factored out. For simulations they used the excess DOS, as it gives shorter acceptance formulas. In contrast, Yan *et al.* [8] provide a reference for the use of configurational DOS simulations. Both methods differ in the prefactors applied to the acceptance probabilities of the insertion and deletion (removal) moves. Using the configurational DOS the acceptance criteria for particle insertions and removals are

$$a((E_i,N) \to (E_j,N+1)) = \min\left[1, \frac{V}{(N+1)\Lambda^3} \frac{\Omega(E_i,N)}{\Omega(E_j,N+1)}\right] \tag{2}$$

and

$$a((E_i,N) \to (E_j,N-1)) = \min\left[1, \frac{N\Lambda^3}{V} \frac{\Omega(E_i,N)}{\Omega(E_j,N-1)}\right]. \tag{3}$$

Here Λ denotes the de Broglie thermal wavelength. The excess DOS acceptance criteria, as given by Shell *et al.* [7], are

$$a((E_i,N) \to (E_j,N+1)) = \min\left[1, \frac{\Omega_{\text{ex}}(E_i,N)}{\Omega_{\text{ex}}(E_j,N+1)}\right] \tag{4}$$

and

$$a((E_i,N) \to (E_j,N-1)) = \min\left[1, \frac{\Omega_{\text{ex}}(E_i,N)}{\Omega_{\text{ex}}(E_j,N-1)}\right]. \tag{5}$$

Configurational and excess DOS are related by

$$\Omega(N,V,E) \propto \frac{V^N}{N!}\Omega_{\text{ex}}(N,V,E), \tag{6}$$

where the factor $V^N/N!$ is related to the partition function of an ideal gas [18], with $N!$ being attributed to the indistinguishability of the particles. The DOS is updated similarly to the canonical ensemble case:

$$\Omega_{t+1}(E,N) = \Omega_t(E,N) \cdot f. \tag{7}$$

B. The par$Q$ method

The par$Q$ method is a transition matrix method using appropriately collected transition frequencies between energy macrostates for determining the DOS. These are transformed into an "infinite temperature transition matrix" Q, which was used originally in Ref. [5] to determine thermodynamic equilibrium properties.

Here we follow Refs. [6,19] to derive the relevant relation between Q and the DOS $\Omega(E_i)$:

$$\Omega(E_j) = \sum_i Q_{ij}\Omega(E_i); \tag{8}$$

i.e., the DOS $\Omega(E_i)$ is the left eigenvector of Q. Let us assume that we want to model a thermalization process on the macrostates using a master equation for a random walker performing a walk in energy space. Its transition probability $\Gamma_{ij}(T)$ from energy E_i to energy E_j is given as

$$\Gamma_{ij}(T) = Q(E_i \to E_j)\, a(E_i \to E_j,T), \tag{9}$$

where the acceptance probability for the Metropolis criterion is $a(E_i \to E_j,T) = \min[1, e^{-(E_j - E_i)/(k_B T)}]$. Then the probability $p(E_i,t)$ to be in a macrostate E_i at time t obeys

$$p(E_j,t+1) = \sum_{i=1}^{N_E} p(E_i,t)\Gamma_{ij}(T), \tag{10}$$

where N_E is the number of energy values (bins) considered. The stationary distribution $p^*(E)$ of Eq. (10) is the left eigenvector to the largest eigenvalue 1 of $\Gamma_{ij}(T)$ and must be equivalent to the Boltzmann distribution

$$p^*(E_j) = \frac{1}{Z(T)}\Omega(E_j)\mathrm{e}^{-\beta E_j}. \tag{11}$$

Thus, for $t \to \infty$ we can insert the stationary distribution into Eq. (10) and obtain

$$\Omega(E_j)\mathrm{e}^{-\beta E_j} = \sum_{i=1}^{N_E} \Gamma_{ij}(T)\Omega(E_i)\mathrm{e}^{-\beta E_i}. \tag{12}$$

Then taking the limit $T \to \infty$ sets the acceptance probability $a(E_i \to E_j,T) = 1$ and thus leads directly to the central relation (8), which contains only the *proposal* probabilities. As a consequence, having knowledge of the matrix Q allows one to calculate the DOS and thus thermodynamic properties of the system.

The problem of obtaining Q or rather a good estimate of it is now solved by performing a canonical Monte Carlo simulation, in which moves to neighboring microstates are proposed and then accepted or not depending on the acceptance probability. Above we showed that only the proposal probability is of relevance, and thus during the simulation all *proposed* moves are counted in a matrix C:

$$C_{ij} = C_{ij} + 1. \tag{13}$$

At the end of the simulation the created counting matrix is normalized rowwise:

$$Q_{ij} = \frac{C_{ij}}{\sum_k C_{ik}}, \tag{14}$$

which creates the stochastic matrix Q, i.e., the infinite temperature transition matrix.

As the transition matrix Q has a predefined energy range one needs to be cautious while handling moves leaving this range. Every move leading to an E_j outside of our energy range has to be counted to the diagonal element [17] according to

$$C_{ii} = C_{ii} + 1. \tag{15}$$

If a move already starts outside of the considered energy range, then it is ignored completely.

In order to obtain a good Q estimate it is important that the state space is sampled in a representative fashion. Usually simulating at a fixed temperature samples only a narrow part of the state space. Thus algorithms originally designed for optimization, like simulated annealing [5,6] or threshold accepting [20], have been used in previous work. In their original publication Heilmann *et al.* [6] applied simulated annealing with linear and exponential schedules to achieve a broad sampling of the energy space of an Ising spin glass. Another approach dubbed WL-TM is proposed by Shell *et al.* [21], where the Wang-Landau [1,2] method is used to achieve broad sampling of Lennard-Jones and Ising systems. Fenwick [22] presented a third method, using the replica exchange (parallel tempering) method to run the simulation in parallel at different temperatures, which are selected in a way that the resulting energy distributions overlap.

III. THE PARQ METHOD FOR THE GRAND CANONICAL JDOS

We now present the extension of the par$Q$ method, which allows us to determine the JDOS. Contrary to the canonical ensemble, where energy is the only macroscopic variable, we now have energy E and number of particles N as varying quantities. The resulting joint DOS $\Omega(E,N)$ is a function of both state variables. This makes the assembly of the Q matrix in the grand canonical ensemble μVT less intuitive and one has to give some thought about correct sampling, broad state space exploration across the whole particle number range and the in-memory matrix layout.

Considering a system limited to $n = 100$ particles with the energy range being split up into 1000 bins the resulting transition matrix would have $(100 \times 1000)^2 = 10^{10}$ entries. By using the restriction made by grand canonical particle insertion and removal moves, where only one particle can be added or deleted at a time, we can reduce the matrix size to a banded block matrix with, e.g., $98\times3\times1000^2 + 2\times2\times1000^2 = 298\times10^6$ entries [19]. In this case the full Q matrix has a structure as displayed below:

$$Q = \begin{bmatrix} Q^E_{1,1} & Q^E_{1,2} & & & & 0 \\ Q^E_{2,1} & Q^E_{2,2} & Q^E_{2,3} & & & \\ & Q^E_{3,2} & Q^E_{3,3} & Q^E_{3,4} & & \\ & & \ddots & \ddots & \ddots & \\ & & & Q^E_{n-1,n-2} & Q^E_{n-1,n-1} & Q^E_{n-1,n} \\ 0 & & & & Q^E_{n,n-1} & Q^E_{n,n} \end{bmatrix} \tag{16}$$

with Q^E being a matrix of size $N_E \times N_E$, where N_E is again the number of energy bins. Note that the number of nonzero entries in the matrix is crucial for the execution times of the DOS calculations, as we use sparse matrix algorithms. However, we stress that the number of nonzero elements depends on the length of the data-acquisition runs and the type of system considered, and thus the overall convergence times can vary considerably.

Each pair of energy and number of particles (E,N) can be seen as a separate macrostate. Therefore we have transitions from $(E,N)_i$ to $(E,N)_j$. Each proposed transition is counted in the same fashion as in the canonical ensemble. As for the canonical case the method is independent of the acceptance probability of the underlying sampling scheme, as long as the proposal probability $q(i \to j)$ is unchanged (or, in other words, as long as the move class is preserved).

IV. A METHOD FOR THE COMPUTATION OF THE JOINT DENSITY OF STATES FROM SPARSE TRANSITION MATRICES

Working in the grand canonical ensemble or the isobaric-isothermal ensemble, or in general having other order parameters besides the temperature, increases the size of the transition matrix enormously. Typically, matrices are of size $50\,000\times50\,000$ and larger as well as sparse. The goal is now to determine the JDOS from this large matrix. One way to do this is by computing its eigenvector to the eigenvalue one.

Although the sparsity of the matrix lends itself to the application of the power iteration method for calculating the eigenvector and thus the JDOS, it turns out not to be the optimal choice. One problem is that the number of iterations needed for the method to converge increases with the number of rows, and the time it takes to perform a single iteration increases as well. Thus, calculating the eigenvector of a 500 × 500 matrix is a matter of seconds on a single processor, whereas it can be a matter of hours for large grand canonical systems.

Another method to obtain the JDOS from Q, proposed by Wang and Swendsen [3], is based on the minimization of detailed balance deviations, i.e., the minimization of the expression

$$\sigma_{\mathrm{tot}}^2 = \sum_{i,j} \frac{\left(\ln\Omega_i - \ln\Omega_j + \ln\frac{Q_{ij}}{Q_{ji}}\right)^2}{\sigma_{ij}^2}. \tag{17}$$

Instead of using the empirically estimated variances as proposed by Wang and Swendsen we use the sophisticated weights proposed by Shell *et al.* [21], which are given by

$$\sigma_{ij}^2 = C_{ij}^{-1} + C_{ji}^{-1} + \left(\sum_k C_{ik}\right)^{-1} + \left(\sum_k C_{jk}\right)^{-1}. \tag{18}$$

Instead of a direct minimization of (17) with respect to $\ln\Omega_i$ we make use of the fact that minimizing σ_{tot}^2 is equivalent to finding approximate solutions to an overdetermined equation system of the form

$$M \cdot x = b. \tag{19}$$

Here the rectangular matrix M contains as many rows as there are pairs (Q_{ij}, Q_{ji}). The row for the kth pair is

$$M_{ki} = \sigma_{ij}^{-1} \quad \text{and} \quad M_{kj} = -\sigma_{ij}^{-1}, \tag{20}$$

which makes the matrix M highly sparse. The corresponding entry in vector b is given by

$$b_k = -\sigma_{ij}^{-1} \ln\frac{Q_{ij}}{Q_{ji}}. \tag{21}$$

Standard implementations in libraries to solve the above problem like the *GNU Scientific Library* [23] assume that M is a dense matrix and are therefore not helpful due to their run time and the amount of memory needed. Hence methods for handling these sparse matrices are needed.

One existing method that is able to handle such matrices is the *LeastSquares* command of Mathematica setting the parameter “Method” to “Direct”. We will refer to this method as MLS.

Here we propose another method based on Eq. (19) and on a fast, Krylov method-based, linear equation system solver. We multiply Eq. (19) by M^{T} to obtain

$$(M^{\mathrm{T}}M)x = M^{\mathrm{T}}b. \tag{22}$$

Although in general solving this equation may be prone to high numerical errors, as $M^{\mathrm{T}}M$ typically has a large condition number, we found that choosing the right solver allows for a fast and still high-quality calculation of the JDOS.

The resulting matrix M typically has a size in the order of 500 000 × 50 000 or larger, with only two entries per row. Performing the multiplication $M^{\mathrm{T}}M$ reduces the size back to the size of the original square transition matrix. The resulting equation system can then be solved in a matter of seconds or minutes.

We will refer to our method as efasTM and emphasize that it can be applied to any transition matrix inversion.

V. JOINT DENSITY OF STATES OF A LENNARD-JONES SYSTEM IN THE GRAND CANONICAL ENSEMBLE

In this section we analyze the performance of efasTM with respect to the quality of the obtained JDOS as well as with respect to the run times needed as compared to other methods. In order to do so we determine the JDOS for a Lennard-Jones system using different techniques.

The particles in the system interact with each other via the Lennard-Jones potential

$$V(r_{ij}) = 4\epsilon\left[\left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^{6}\right], \tag{23}$$

where ϵ sets the energy and σ the length scale. It is capable of reproducing the complete thermodynamic behavior of classic fluids while being one of the simplest models available. The Lennard-Jones system exhibits solid-liquid [24] and vapor-liquid [25] phase transitions as well as a Mackay/anti-Mackay transition [26,27] at low temperatures. The latter can be observed for clusters of different sizes [28–30]. Thereby the cluster overlayer melts, changing its Mackay packaging [31] to a less dense liquid-like packaging.

The Lennard-Jones potential $V(r)$ used here and in the simulations below is cut off at radius $r_{\mathrm{c}} = 2.5\sigma$. The potential is neither shifted by the energy at the cutoff radius $V(r_{\mathrm{c}})$ nor tail-corrected. From here on we choose ϵ and σ as the units of our energy and length scales, respectively.

We performed simulations in the grand canonical μVT ensemble, which used moves in energy space (i.e., particle displacements) as well as particle insertions and removals. The number of particles N in a fixed volume of size 5^3 was allowed to fluctuate between 1 and 110 particles. Periodic boundary conditions were used.

The overall energy range was set to $E \in [-700, 10]$ and split into 500 bins. In addition per-particle energy ranges were bounded (see Ref. [19]) in order to keep the Q-matrix size under control.

An implementation of the Wang-Landau algorithm was used to randomly walk through the system’s state space and to achieve a broad sampling. As the standard flatness condition is not functional for the structure of the JDOS a slightly modified flatness condition, which checks whether the number of visited bins stays constant for 10 000 time steps and for a minimum number of visits to each bin, has been used. After 2×10^9 time steps and 14 refinements, reaching $f = 6.10352 \times 10^{-5}$, the resulting JDOS was determined at the end of the Wang-Landau data acquisition. We made no early attempt to determine the the JDOS from the collected C matrix as it would suffer from the inaccuracies of the transition matrix as described in Ref. [21]. During the run, the proposed moves were monitored and stored in a C matrix, from which the Q matrix was determined. We implemented the combination of Wang-Landau algorithm and par$Q$ transition matrix method in the open source Monte Carlo simulation tool *MCCCS Towhee* [32].

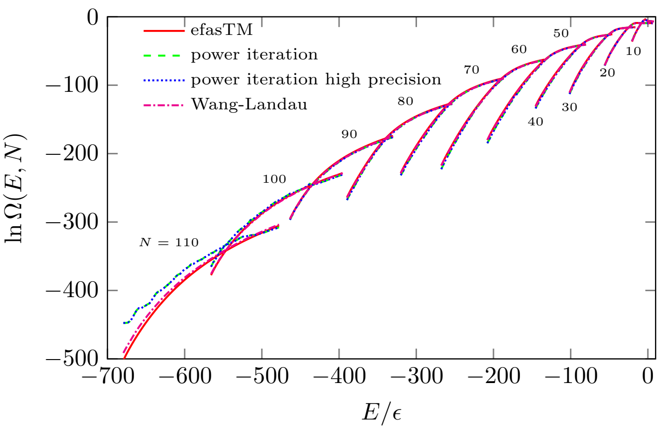

FIG. 1. Density of states of a Lennard-Jones system in the grand canonical ensemble. The simulation covered the energy range $E \in [-700, 10)$ and the particle number range $N \in [1, 110]$. Additionally the energy range per particle number has been restricted (see Ref. [19] for details). For each data set a selection of particle numbers $N = 10, 20, \ldots, 110$ is shown from right to left in increasing order. Wang-Landau sampling has been used to achieve broad sampling. The corresponding DOS is shown for reference. Additionally, transition data have been recorded, which has been analyzed with different methods. First, the power iteration at double precision and at about four times the precision of "double precision" has been used. Both methods give equal results and match the Wang-Landau DOS up to $N = 90$. For $N \in \{100, 110\}$ strong deviations are visible at the low energy bound. Using the efasTM method gives results comparable to Wang-Landau.

In Fig. 1 we present a comparison of the DOS from this simulation of Lennard-Jones particles in the μVT ensemble. The obtained Wang-Landau result for the JDOS has been included for comparison (violet line). The transition matrix recorded during the simulation has been evaluated using the efasTM method (red line) and the power iteration method in machine precision (green line) as well as using arbitrary precision arithmetics with a 64 digit precision (about four times of machine precision, blue line).

We find that the precision used to perform the power method has no influence on the outcome. Both variants give results on par with densities of states obtained from the Wang-Landau method and the efasTM method for particle numbers up to $N = 90$.

Focusing on larger N in Fig. 1 we observe that this agreement between the JDOS is lost; instead a clear deviation in the JDOS at low energies for the power iteration occurs. In contrast, looking at the efasTM results, we only find a slight differences for $N = 110$. In conclusion we find excellent agreement between the Wang-Landau and the efasTM results. One possible explanation for the quality of the efasTM approach is, that the raw data of the Q matrix are modified with the weights given by Shell *et al.* [21] [see Eq. (18)]. Besides differences in the quality of the JDOS we also find large differences between efasTM and the power iteration with respect to the computing times needed to obtain those results.

Table I gives an overview of how much CPU time was needed in total, incorporating parallel execution of parts of the algorithm, as well as the wall time needed altogether. The computations have been performed using the highly optimized algorithms of *Mathematica*. We find, that the efasTM method performs an order of magnitude faster than the MLS method. Looking at the total CPU time the speedup is nearly two orders of magnitude. For the power iteration we find that the efasTM method is more than two orders of magnitude faster.

TABLE I. Timings of three different methods to calculate the DOS from large sparse transition matrices. Wall time and total CPU time differ, as some parts of the algorithms are executed in parallel. Note that efasTM outperforms the other two methods by at least one order of magnitude.

Method	Wall time	Total CPU time
efasTM	35 s	38 s
MLS	484 s	2390 s
Power iteration	4263 s	4845 s

To analyze the scaling properties of the efasTM algorithm further we determined the execution times as a function of the number of nonzero Q-matrix elements. These are shown in Fig. 2.

As the time for the data acquisition for the Q matrix was typically about an order of magnitude larger then the time for obtaining the DOS from the Q matrix using the power iteration method the time savings in our case was about 10%. However, we stress that the relation between data acquisition time and DOS calculation time depend very much on the implementation and parallelization.

Above we judged the quality of the JDOS results obtained by efasTM by comparing it with the JDOS from the Wang-Landau method. In principle it would of course be better to check which of the results is closer to the true DOS. Unfortunately we cannot resort to such a comparison with exact results, as those do not exist. As an additional check we thus compare quantities computed from the joint DOS to literature data. Here we focus on the liquid and vapor phase transition of the Lenard-Jones system. To do so, we below

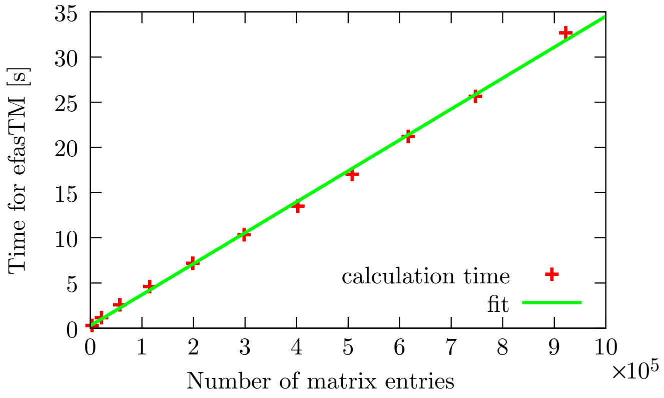

FIG. 2. The execution time for determining the JDOS from the Q matrix according to the efasTM method is shown as a function of number of nonzero elements in the Q matrix. The data show a clear linear relationship with a slope of 3.42409×10^{-5} and a negligible axis intercept. Note that the number of nonzero elements depends on the length of the Wang-Landau data-acquisition run.

present appropriate formulas and algorithm to determine the liquid and vapor coexistence lines.

VI. CALCULATING PHASE COEXISTENCE PROPERTIES

Being able to predict the outcomes of measurements is of huge interest in material research in industry and science. Having a precise estimate of the DOS available alleviates this task. The formulas below are taken from Yan *et al.* [8] and use the configurational DOS.

For instance, having obtained Ω as a function of energy E and particle number N, the grand canonical partition function

$$\Xi(T,\mu) = \sum_N \sum_E \Omega(E,N)\,\mathrm{e}^{-\beta E+N\beta\mu} \tag{24}$$

can be calculated as a function of temperature T and chemical potential μ. From this, we can obtain quantities like the the mean particle number and its second moment:

$$\langle N\rangle = \Xi^{-1}\sum_N \sum_E N\,\Omega(E,N)\,\mathrm{e}^{-\beta E+N\beta\mu}, \tag{25}$$

$$\langle N^2\rangle = \Xi^{-1}\sum_N \sum_E N^2\,\Omega(E,N)\,\mathrm{e}^{-\beta E+N\beta\mu}, \tag{26}$$

both being functions of T and μ as well.

A liquid and a vapor phase are in phase coexistence, if the pressure in both phases is equal, i.e., $p_{\mathrm{vap}} = p_{\mathrm{liq}}$. The pressure is a function of the logarithm of the grand canonical partition function, i.e.,

$$p(T,\mu) = \frac{\mathrm{k_B}T}{V}\log \Xi(T,\mu). \tag{27}$$

To separate the two phases we have to find an N_{mid} such that the pressure can be separated into

$$p_{\mathrm{vap}}(T,\mu) = \frac{\mathrm{k_B}T}{V}\log \sum_{N\leqslant N_{\mathrm{mid}}} \sum_E \Omega(E,N)\,\mathrm{e}^{-\beta E+N\beta\mu} \tag{28}$$

and

$$p_{\mathrm{liq}}(T,\mu) = \frac{\mathrm{k_B}T}{V}\log \sum_{N> N_{\mathrm{mid}}} \sum_E \Omega(E,N)\,\mathrm{e}^{-\beta E+N\beta\mu}. \tag{29}$$

To find N_{mid} we define the probability

$$P(N,T,\mu) = \Xi^{-1}\sum_E \Omega(E,N)\,\mathrm{e}^{-\beta E+N\beta\mu} \tag{30}$$

to observe particle number N at a fixed T and μ independent of E. Now, for any given temperature we have to guess an initial value for μ such that $p(N)$ exhibits two distinct peaks. Then, the local minimum in between the two peaks can be determined, i.e., $N_{\mathrm{mid}} = \mathrm{argmin}_N\, p(N)$ under the given constraints. Next, μ has to be tuned to satisfy $p_{\mathrm{vap}} = p_{\mathrm{liq}}$ while recalculating N_{mid} in every optimization step. The procedure ends when a stable μ_0 has been reached.

The coexistence densities may then be obtained via

$$\rho_{\mathrm{vap}}(T) = \frac{1}{V}\frac{\sum_{N\leqslant N_{\mathrm{mid}}}\sum_E N\Omega(E,N)\,\mathrm{e}^{-\beta E+N\beta\mu_0}}{\sum_{N\leqslant N_{\mathrm{mid}}}\sum_E \Omega(E,N)\,\mathrm{e}^{-\beta E+N\beta\mu_0}} \tag{31}$$

and

$$\rho_{\mathrm{liq}}(T) = \frac{1}{V}\frac{\sum_{N> N_{\mathrm{mid}}}\sum_E N\Omega(E,N)\,\mathrm{e}^{-\beta E+N\beta\mu_0}}{\sum_{N> N_{\mathrm{mid}}}\sum_E \Omega(E,N)\,\mathrm{e}^{-\beta E+N\beta\mu_0}}, \tag{32}$$

where the chemical potential μ_0 depends on T and is obtained from the previous procedure.

We will now apply this technique of calculating coexistence curves from the JDOS by using the JDOS data obtained above for the Lennard-Jones system. The results are shown in Fig. 3. Here the left figure shows a contour plot of $P(\rho,T)$ based on Eq. (30), using $\rho = N/V$, at the chemical potential μ_0 of phase coexistence. The colors scale linearly from blue $(P(\rho,T)=0)$ to red $(P(\rho,T)=0.04)$, whereas white indicates larger values of $P(\rho,T)$. The DOS used is the one obtained by the efasTM method, represented by the red curves

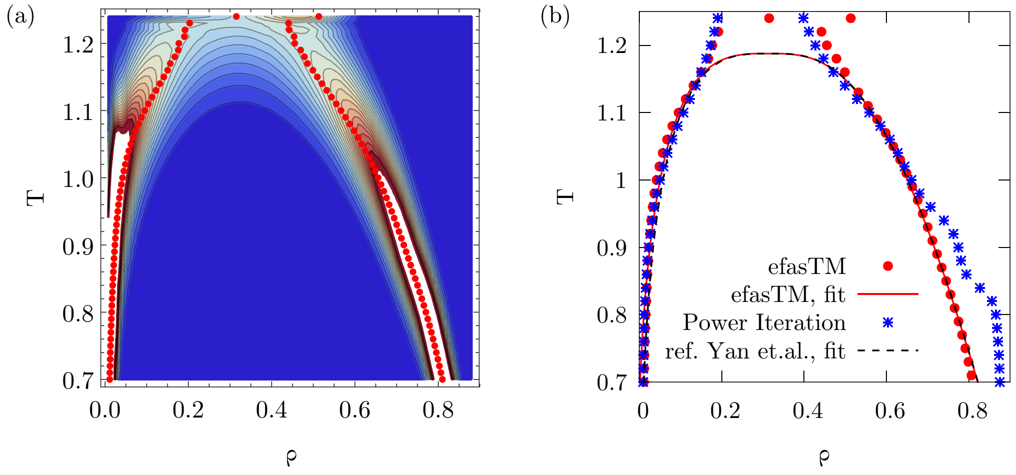

FIG. 3. The left frame (a) shows a density plot of the function $P(\rho,T)$ [see Eq. (30)] for DOS data obtained via efasTM. For every value of T the chemical potential μ has been tuned to reach phase coexistence. The colors scale linearly from blue $(P(\rho,T)=0)$ to red $[P(\rho,T)=0.04]$, whereas white indicates larger values of $P(\rho,T)$. The red points lying on top are the mean densities of the vapor and liquid phases. The two points at $T = 1.24$ K indicate that the algorithm failed to find the correct density for separating liquid and vapor phase. In the right frame (b), the red points correspond to those shown in the left plot. The blue stars correspond to DOS data, obtained via power iteration from the same transition matrix as the red points. We find a strong deviation in the liquid region for $T < 1$, which can be traced back to the deviations in the DOS. The red line is an Ising form fit to the red points, whereas the black dashed line is a fit to data from Yan *et al.* [8].

in Fig. 1. The red dots indicate the coexistence densities ρ_{vap} and ρ_{liq} determined according to Eqs. (31) and (32). Above the critical temperature $T_{\text{c}} = 1.1876(3)$ [33] known from other methods, the distribution $P(N,T,\mu)$ in principal should loose its bimodality. However, due to numerical fluctuations as well as finite size effects the algorithm still finds local maxima of the probability $P(N,T,\mu)$ above T_{c}. The two out-of-line points at $T = 1.24$ indicate these minima are spurious.

In the right frame of Fig. 3 the red points correspond to those in the left frame. The blue points are obtained by applying the phase coexistence calculation to the power iteration data (blue dotted curves of Fig. 1). We find that the deviations already found in the previous figure lead to large deviations in the points representing the liquid phase.

The lines are obtained by fitting the function [25,34]

$$\rho_{\pm} = \rho_c + a\left|\frac{T - T_{\text{c}}}{T_{\text{c}}}\right| \pm b\left|\frac{T - T_{\text{c}}}{T_{\text{c}}}\right|^{\beta}, \qquad (33)$$

with density ρ_{c} at critical temperature T_{c} and free parameters a, b, and β to the data. For β we use the 3D Ising order-parameter exponent $\beta = 0.3258$ [35]. For the critical temperature we use the result of Wilding *et al.* [33], who determined it to be $T_{\text{c}} = 1.1876(3)$ for a system of infinite size by finite size scaling. The remaining parameters ρ_{c}, a, and b have been obtained via numerical fitting.

The red line in Fig. 3 is a fit to the efasTM data (red points). For reference, a fit to phase coexistence data from Yan *et al.* [8] has been added (black dashed line). We find that both coincide in the fluid region very well and differ only slightly in the vapor region. Hence, we find that the par$Q$ method in combination with the Wang-Landau sampling for the grand canonical ensemble can produce reliable results, on par with literature data obtained by pure Wang-Landau sampling. The par$Q$ approach has the additional benefit of much easier parallelization than the windowing or stratification approaches used for Wang-Landau simulations. One can perform any number of independed simulations in parallel and combine the resulting C matrices to obtain a single combined Q matrix.

VII. SUMMARY

One effective method to determine thermo-physical properties of fluids is based on DOS methods. These methods allow access to those properties including phase transitions as they provide information on the material at different temperatures and pressures. In order to achieve this one needs to know the JDOS, i.e., the DOS as a function of the energy and the density (or particle number). Determining the JDOS is numerically demanding with respect to accuracy as well as run time. We presented a transition matrix-based method by extending the par$Q$ method to grand canonical ensembles. The advantage of the method compared to the classical Wang-Landau histogram method is that data from nonconverged runs can be used. In addition data from different state space exploration methods can be combined, allowing a flexible approach with adaptive changes in the exploration method without loosing data. We developed the efasTM method as a method for obtaining the JDOS from the transition matrix data, which for the Lennard-Jones example system analyzed showed run time up to a factor of 100 faster than other standard methods. An interesting open question is whether these speed-ups can be sustained also for other systems. As a quality check we compared our results for the JDOS with Wang-Landau data and found a very good agreement. As a second quality check we compared phase coexistence data obtained from the JDOS with reference data from Yan *et al.* and found again excellent agreement. Thus the par$Q$ method for grand canonical ensembles together with efasTM presents a viable alternative for determining the JDOS, especially as it allows an easy parallelization and an efficient usage of known state space data.

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