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Citation: The Journal of Chemical Physics **147**, 054105 (2017); doi: 10.1063/1.4996759
View online: http://dx.doi.org/10.1063/1.4996759
View Table of Contents: http://aip.scitation.org/toc/jcp/147/5
Published by the American Institute of Physics

THE JOURNAL OF CHEMICAL PHYSICS **147**, 054105 (2017)

Temperature extrapolation of multicomponent grand canonical free energy landscapes

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(Received 12 May 2017; accepted 18 July 2017; published online 7 August 2017)

We derive a method for extrapolating the grand canonical free energy landscape of a multicomponent fluid system from one temperature to another. Previously, we introduced this statistical mechanical framework for the case where kinetic energy contributions to the classical partition function were neglected for simplicity [N. A. Mahynski *et al.*, J. Chem. Phys. **146**, 074101 (2017)]. Here, we generalize the derivation to admit these contributions in order to explicitly illustrate the differences that result. Specifically, we show how factoring out kinetic energy effects *a priori*, in order to consider only the configurational partition function, leads to simpler mathematical expressions that tend to produce more accurate extrapolations than when these effects are included. We demonstrate this by comparing and contrasting these two approaches for the simple cases of an ideal gas and a non-ideal, square-well fluid. [http://dx.doi.org/10.1063/1.4996759]

I. INTRODUCTION

Monte Carlo (MC) simulations are a well-established technique for computing the thermodynamic properties of fluid phases.[1–3] Grand canonical Monte Carlo (GCMC) simulations consider systems at a fixed volume which may exchange mass and energy with their surroundings, and are particularly useful for computing fluid phase coexistence of subcritical bulk fluids. Although numerous other MC approaches have been developed for this application,[1–4] when combined with flat-histogram methods, GCMC can be a particularly efficient method for computing thermodynamic properties of multicomponent fluids.[5–7] In the absence of an applied sampling bias, the macrostate probability distributions from GCMC simulations at different imposed chemical potentials and temperatures may be combined and then coupled to histogram reweighting approaches to predict properties at other conditions.[1,8–11] A macrostate is defined by the instantaneous value of the extensive property conjugates of chemical potential and temperature, i.e., the number of molecules of each component present and the system's internal energy. However, in general, reweighting involves the discretization of the energy portion of a system's macrostate space; neither the bounds nor the resolution of this space is generally known *a priori*, and a poor choice can lead to erroneous results. Furthermore, the (hyper)volume of phase space grows geometrically with the number of components present, quickly making this intractable for multicomponent fluids.

As an alternative approach, we recently developed a technique to extrapolate a GCMC macrostate distribution from one temperature to another by expanding the distribution as a Taylor series at each macrostate.[12] This does not require any discretization of the energy portion of phase space, trivially generalizes for multicomponent fluids,[6] and improves the computational efficiency of biased GCMC methods when studying fluid phase thermodynamics over a range of temperatures. Furthermore, we have demonstrated that the derivatives involved in these Taylor series expansions are straightforward to calculate by collecting readily available quantities within each flat-histogram GCMC simulation. Thus, it requires essentially no additional effort to implement. Previously, we derived this statistical mechanical framework when the kinetic energy of the fluid's components had been factored out of the system's classical partition function and ignored. In other words, only the configurational partition function was considered.

For reasons we will subsequently discuss, this significantly reduces the complexity of the mathematical expressions involved in our extrapolation approach. At fixed temperature, the choice to include or neglect these effects does not influence a system's extensive thermodynamic properties (except the internal energy itself); however, when using this temperature extrapolation method, there are significant ramifications that we describe herein. Generally speaking, we find that our extrapolation approach is more accurate when these effects are neglected, as in previous work.[12] Here we provide the mathematical basis for this choice and provide the equations necessary for the application of our method in the case that kinetic effects are included.

This paper is organized as follows. In Sec. II, we discuss the thermodynamic ensembles involved in our multicomponent sampling approach and describe the extrapolation method itself and the flat-histogram MC simulations we use to illustrate our method. Subsequently, in Sec. III, we derive the

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statistical mechanical expressions for the thermodynamic derivatives necessary to perform the extrapolation. This highlights the implementation differences between when kinetic energy effects are accounted for and when they are neglected. Section IV contains results which exemplify the differences between the two cases for an ideal gas and for a non-ideal, square-well fluid. We conclude in Sec. V by summarizing the results and providing guidelines for practitioners to implement our method.

II. METHODS

A. The isochoric semigrand ensemble

Consider a k-component system in the grand canonical ensemble, where the chemical potentials, $\vec{\mu} = (\mu_1, \mu_2, \ldots, \mu_k)$, volume, V, and temperature, T, are fixed. The grand canonical partition function may be written as

$$\Xi(\vec{\mu}, V, \beta) = \sum_{N_1} \cdots \sum_{N_k} \exp\left(\beta \sum_{i=1}^{k} \mu_i N_i\right) Q, \tag{1}$$

where Q is the canonical partition function, $\beta \equiv 1/k_B T$ (k_B is the Boltzmann constant), and N_i is the number of molecules of species i. Here, we focus on the case when the total particle number, $N_{tot} = \sum_{i=1}^{k} N_i$, is used as the order parameter to define a system's macrostate. This order parameter has often proven useful for studying first order phase transitions in multicomponent fluids.[6,12] Extensions to other order parameters may also be derived by following the procedure we have outlined in this and previous work[12] but are beyond the scope of this paper. Through a change of variables, one may express Eq. (1) as[6]

$$\begin{aligned}\Xi(\vec{\mu}, V, \beta) &= \sum_{N_{tot}} \exp(\beta \mu_1 N_{tot}) \\ &\quad \times \left[\sum_{N_2} \cdots \sum_{N_k} \exp\left(\beta \sum_{i=2}^{k} \Delta\mu_i N_i\right) Q\right] \\ &= \sum_{N_{tot}} \exp(\beta \mu_1 N_{tot})\, \Upsilon(N_{tot}; \Delta\vec{\mu}, V, \beta),\end{aligned} \tag{2}$$

where $\Delta\mu_i \equiv \mu_i - \mu_1$, and $\Upsilon(N_{tot}; \Delta\vec{\mu}, V, \beta)$ is the isochoric semigrand partition function,

$$\Upsilon(N_{tot}; \Delta\vec{\mu}, V, \beta) = \sum_{N_2} \cdots \sum_{N_k} \exp\left(\beta \sum_{i=2}^{k} \Delta\mu_i N_i\right) Q. \tag{3}$$

Thus, the probability of a given macrostate, $\Pi(N_{tot})$, may be expressed as

$$\ln \Pi(N_{tot}) = \beta \mu_1 N_{tot} + \ln \Upsilon - \ln \Xi. \tag{4}$$

From standard histogram reweighting techniques,[1] this distribution for some μ_1 may be estimated from a distribution measured at the same temperature, volume, and $\Delta\vec{\mu} = (\Delta\mu_2, \Delta\mu_3, \ldots, \Delta\mu_k)$ but a different μ_1^0 as follows:

$$\begin{aligned}\ln \Pi(N_{tot}; \mu_1, \Delta\vec{\mu}) &= \ln \Pi(N_{tot}; \mu_1^0, \Delta\vec{\mu}) \\ &\quad + \beta(\mu_1 - \mu_1^0) N_{tot}.\end{aligned} \tag{5}$$

In the vicinity of a first order transition between fluid phases with low and high overall densities, the macrostate distribution displays multiple peaks, each corresponding to a given phase, delineated by a trough between each of them.[5,6] Once the macrostate distribution is known, one may compute a grand canonical ensemble-averaged thermodynamic property, $\langle X \rangle$, of some phase α,

$$\langle X \rangle = \frac{\sum_{N_{tot} \in \alpha} \Pi(N_{tot}) X(N_{tot})}{\sum_{N_{tot} \in \alpha} \Pi(N_{tot})}, \tag{6}$$

where X is some extensive property measured as a function of N_{tot}. Furthermore, the pressure, P, of the system is known from

$$P^{\alpha} V \beta = \ln\left(\sum_{N_{tot} \in \alpha} \Pi(N_{tot})\right) - \ln \Pi(0). \tag{7}$$

Coexistence between phases can be found by searching for the condition corresponding to equal pressures since by definition, the phases already have the same imposed temperature and chemical potential(s) in a GCMC simulation.

B. The canonical partition function

Thus, $\ln \Pi(N_{tot})$ is a function of Υ and Ξ, which both depend on the canonical partition function

$$Q_{tot} = \frac{1}{\prod_{i=1}^{k} h^{dN_i} N_i!} \int \exp\left(-\beta \mathcal{H}(\vec{q}, \vec{r})\right) d\vec{r} d\vec{q}, \tag{8}$$

where $\mathcal{H}$ is the Hamiltonian of the system, d is the system's spatial dimensionality, and h is Planck's constant. In this work, we exclusively focus on $d = 3$. For simplicity, we also assume that particles are monatomic and have no internal degrees of freedom, although this does not affect the generality of our conclusions.

We denote the momenta degrees of freedom for each particle present in all dimensions by $\vec{q}$ and similarly the configurational degrees of freedom as $\vec{r}$. In the classical limit, kinetic and potential energy contributions may be decoupled such that $\mathcal{H}(\vec{q}, \vec{r}) = U_p(\vec{q}) + U_k(\vec{r})$.[2] Therefore, we can express the total canonical partition function as the product of the partition functions resulting from the integration of the configurational (potential energy) and momenta (kinetic energy) degrees of freedom such that $Q_{tot} = Q_p Q_k$, where

$$Q_p = \frac{1}{\prod_{i=1}^{k} N_i!} \int \exp\left(-\beta U_p(\vec{r})\right) d\vec{r}. \tag{9}$$

Because the kinetic energy operator is a quadratic function of the momenta of all particles in each spatial dimension, Q_k may be evaluated analytically,

$$\begin{aligned}Q_k &= \frac{1}{\prod_{i=1}^{k} h^{dN_i}} \int \exp\left(-\beta U_k(\vec{q})\right) d\vec{q} \\ &= \frac{1}{\prod_{i=1}^{k} \Lambda_i^{dN_i}}.\end{aligned} \tag{10}$$

Here, $\Lambda_i = \sqrt{h^2/(2\pi m_i k_B T)}$ is the thermal de Broglie wavelength and m_i is the mass of species i. Consequently, at a given temperature, Q_k represents a constant multiplier on Q_p. Thus, one may proceed with a GCMC simulation according to one of two broad approaches. One the one hand, kinetic contributions may be included such that the total partition function ($Q = Q_{tot}$) is treated during a MC simulation. On the other hand,

since it is known analytically, the kinetic contributions may be factored out and disregarded, allowing the simulation to exclusively consider the configurational partition function ($Q = Q_p$). Afterwards, one may reintroduce the kinetic effects into any necessary thermodynamic calculations after the simulation has finished.

In previous work, we demonstrated a technique to extrapolate $\ln \Pi(\vec{\Psi})$ from one temperature to another as a function of different order parameters, $\vec{\Psi}$, when Q_k has been neglected.[12] We refer to this approach as "configurational extrapolation" because the simulation considers only the configurational degrees of freedom. Conversely, we refer to the case when kinetic effects are incorporated as "total-energy extrapolation." Here, we illustrate the consequences of including kinetic energy contributions to demonstrate why configurational extrapolation is generally mathematically simpler and computationally more accurate. The key to this is a single partial derivative of Q_{tot}, which is easier to see if we first discretize the integral over a system's degrees of freedom into a sum

$$Q = \sum_{\nu} O(\nu) \exp\left(-\beta \hat{U}(\nu)\right), \tag{11}$$

where ν represents a set of the system's microstates with energy, $\hat{U}(\nu)$, and degeneracy, $O(\nu)$. Consequently, it is clear that

$$\frac{1}{Q}\frac{\partial Q}{\partial \beta} = -U, \tag{12}$$

where U is the average internal energy of the canonical system. We have left Q ambiguous here because Eqs. (11) and (12) hold for both Q_{tot} and Q_p. The energy on the right hand side of these equations is simply different, corresponding to U_{tot} and U_p, respectively. For a system of monatomic particles in the thermodynamic limit,

$$\begin{aligned} \frac{1}{Q_{tot}}\frac{\partial Q_{tot}}{\partial \beta} &= \left(\frac{1}{Q_p}\frac{\partial Q_p}{\partial \beta} + \frac{1}{Q_k}\frac{\partial Q_k}{\partial \beta}\right), \\ U_{tot} &= U_p + U_k \\ &= U_p + \tfrac{d}{2} N_{tot} k_B T. \end{aligned} \tag{13}$$

In what follows, we contrast two cases: (1) total-energy extrapolation, when the kinetic energy contributions are accounted for in a system so that $Q = Q_{tot}$ and $U = U_{tot}$, and (2) configurational extrapolation, when only the configurational partition function is considered such that $Q = Q_p$ and $U = U_p$. Henceforth, when we present U or Q without a subscript, we are implying that the equation it appears in is equally valid for both cases.

C. Extrapolation of the macrostate distribution

As previously shown,[12] one may express the macrostate distribution, $\ln \Pi(N_{tot})$, as a Taylor series in β,

$$\begin{aligned} \ln \Pi(N_{tot};\beta) = \ln \Pi(N_{tot};\beta^0) &+ \left.\frac{\partial \ln \Pi(N_{tot})}{\partial \beta}\right|_{\beta^0} \Delta\beta \\ &+ \frac{1}{2!}\left.\frac{\partial^2 \ln \Pi(N_{tot})}{\partial \beta^2}\right|_{\beta^0} \Delta\beta^2 + \ldots, \end{aligned} \tag{14}$$

where $\Delta\beta \equiv \beta - \beta^0$. Thus, if one can obtain an expression for the requisite derivatives, one can estimate $\ln \Pi(N_{tot})$ at an arbitrary β if it is known at another β^0. In Sec. III, we derive expressions for these derivatives. To evaluate them, all combinations of the products of energy and particle numbers raised to integer powers are measured at each N_{tot} during the simulation at β^0. For example, this includes terms such as $N_1^2 N_2 U^3$, $N_2^2 U$, and U^3. For a desired order of extrapolation, ξ_t, we collect these products in a matrix $Z(N_{tot};\vec{\xi})$ whose elements are specified by the vector $\vec{\xi} = (\xi_1, \ldots, \xi_k, \xi_n, \xi_u)$, where each power in $\vec{\xi}$ is a non-negative integer such that $\xi_i \in [0, \xi_t + 1]$,[12]

$$Z(N_{tot};\vec{\xi}) = N_1^{\xi_1} N_2^{\xi_2} \ldots N_k^{\xi_k} N_{tot}^{\xi_n} U^{\xi_u}. \tag{15}$$

Although the order that Eq. (14) may be calculated up to is given by $\xi_t + 1$, to calculate extensive properties using Eq. (6) at the new temperature, the $Z(N_{tot};\vec{\xi})$ matrix must, in general, also be extrapolated. Following a similar Taylor series approach, this may be done up to order ξ_t.[12] When the $Z(N_{tot};\vec{\xi})$ matrix is averaged over the course of the simulation, its entries reflect averages (moments) in the isochoric semigrand ensemble. In what follows, we denote all such moments with a tilde, $\widetilde{Z}$. From these values, the grand canonical ensemble-averaged quantities, henceforth denoted with brackets,

$$\langle Z \rangle = \frac{1}{\Xi} \sum_{N_{tot}} \exp\left(\beta \mu_1 N_{tot}\right) \widetilde{Z}(N_{tot}) \tag{16}$$

may be calculated using Eq. (6).

During both traditional and flat-histogram GCMC simulations, it is common to record an average of only the potential energy. It is important to emphasize that for total-energy extrapolation to be employed correctly, the energy recorded after each step in the MC simulation must generally be adjusted on-the-fly to include the kinetic contributions. This is because the $Z(N_{tot};\vec{\xi})$ matrix will be used to compute derivatives of the partition functions describing the system, so its entries (which involve energy) must be consistent with the system's canonical partition function (in the case of total-energy extrapolation, Q_{tot}). When N_{tot} is used as a sampling order parameter, it is possible to correct each entry for kinetic energy after the simulation is finished, but it is generally simpler to simply record it on-the-fly.

When considering the differences between including and neglecting kinetic energy, it is convenient to represent the moments in the $Z(N_{tot};\vec{\xi})$ matrix in terms of β-independent and potentially β-dependent factors. The former are denoted collectively as R, and the latter is simply U^{ξ_u}. Thus, one can write

$$Z(N_{tot};\vec{\xi}) = \overbrace{N_1^{\xi_1} N_2^{\xi_2} \ldots N_k^{\xi_k} N_{tot}^{\xi_n}}^{R} U^{\xi_u} = R U^{\xi_u}. \tag{17}$$

Note that in configurational extrapolation, $U = U_p$, which remains independent of β. Furthermore, since N_{tot} is the order parameter and is constant for a given moment in $Z(N_{tot};\vec{\xi})$, the factor involving N_{tot} need not be included during simulation and may simply be added after the simulation has finished. This reduces the size of the $Z(N_{tot};\vec{\xi})$ matrix since the dimensionality of the $\vec{\xi}$ vector is now reduced by one.

D. Simulations

We employed a hybrid Wang-Landau Transition Matrix Monte Carlo (WL-TMMC) simulation approach[13–15] to construct the macrostate distribution for a fluid. Our implementation has already been described in Ref. 12 so we will not reproduce it in detail here. To summarize, an initial Wang-Landau (WL) simulation state is used to obtain a preliminary estimate of the (logarithm of the) macrostate distribution, $\ln \Pi(N_{\text{tot}})$, which is subsequently refined using transition matrix methods.[13,14] In concert, this approach is capable of constructing an accurate macrostate distribution more quickly than either of the two techniques alone.[14]

In this work, we consider two systems as illustrative examples: a single-component ideal gas and a square-well fluid. For the latter, the interparticle potential energy is given by

$$u(r) = \begin{cases} \infty, & r < \sigma \\ -\epsilon, & \sigma \le r < \lambda\sigma \\ 0, & r \ge \lambda\sigma. \end{cases} \tag{18}$$

We set $\epsilon = 1$, $\sigma = 1$, and $\lambda = 1.5$, and use a periodic, cubic simulation cell whose volume is $V = 512\sigma^3$. An ideal gas is simply obtained in the limit that $\lambda\sigma \to 0$.

III. GENERALIZED EXPRESSIONS FOR THE DERIVATIVES

Here we report the necessary derivatives for a second order extrapolation ($\xi_t = 2$) using Eq. (14). We will illustrate the mechanics of the first steps explicitly in order to show how kinetic energy contributions impact the results and leave the higher order derivatives as an exercise to the reader. As will become apparent, all necessary derivatives may be evaluated by using the moments contained within the $Z(N_{\text{tot}}; \vec{\xi})$ matrix.

A. First order terms

The first derivative of Eq. (4) with respect to β is given by

$$\frac{\partial \ln \Pi(N_{\text{tot}})}{\partial \beta} = \mu_1 N_{\text{tot}} + \frac{1}{\Upsilon}\frac{\partial \Upsilon}{\partial \beta} - \frac{1}{\Xi}\frac{\partial \Xi}{\partial \beta}. \tag{19}$$

We therefore require expressions for the derivatives of the two partition functions, Υ and Ξ. Through a simple chain rule, and the application of Eq. (12), we have

$$\begin{aligned} \frac{1}{\Upsilon}\frac{\partial \Upsilon}{\partial \beta} &= \frac{1}{\Upsilon}\sum_{N_2}\cdots\sum_{N_k}\left(\left(\sum_{i=2}^{k}\Delta\mu_i N_i\right)\exp\left(\beta\sum_{i=2}^{k}\Delta\mu_i N_i\right)Q + \exp\left(\beta\sum_{i=2}^{k}\Delta\mu_i N_i\right)\frac{\partial Q}{\partial \beta}\right) \\ &= \frac{1}{\Upsilon}\sum_{N_2}\cdots\sum_{N_k}\left(\left(\sum_{i=2}^{k}\Delta\mu_i N_i - U\right)\exp\left(\beta\Delta\mu_2 N_2\right)Q\right) = \sum_{i=2}^{k}\Delta\mu_i\widetilde{N}_i - \widetilde{U}. \end{aligned} \tag{20}$$

Similarly, for the grand canonical partition function, we arrive at

$$\begin{aligned} \frac{1}{\Xi}\frac{\partial \Xi}{\partial \beta} &= \frac{1}{\Xi}\sum_{N_{\text{tot}}}\sum_{N_2}\cdots\sum_{N_k}\left(\left(\mu_1 N_{\text{tot}} + \sum_{i=2}^{k}\Delta\mu_i N_i\right)\exp\left(\beta\mu_1 N_{\text{tot}} + \beta\sum_{i=2}^{k}\Delta\mu_i N_i\right)Q + \exp\left(\beta\mu_1 N_{\text{tot}} + \beta\sum_{i=2}^{k}\Delta\mu_i N_i\right)\frac{\partial Q}{\partial \beta}\right) \\ &= \frac{1}{\Xi}\sum_{N_{\text{tot}}}\sum_{N_2}\cdots\sum_{N_k}\left(\left(\mu_1 N_{\text{tot}} + \sum_{i=2}^{k}\Delta\mu_i N_i - U\right)\exp\left(\beta\mu_1 N_{\text{tot}} + \beta\sum_{i=2}^{k}\Delta\mu_i N_i\right)Q\right) \\ &= \left\langle \mu_1 N_{\text{tot}} + \sum_{i=2}^{k}\Delta\mu_i N_i - U\right\rangle = \mu_1\langle N_{\text{tot}}\rangle + \sum_{i=2}^{k}\Delta\mu_i\langle N_i\rangle - \langle U\rangle. \end{aligned} \tag{21}$$

Thus, the first derivative of the macrostate distribution at each value of N_{tot} may be expressed as

$$\begin{aligned} \frac{\partial \ln \Pi(N_{\text{tot}})}{\partial \beta} &= \mu_1\left(N_{\text{tot}} - \langle N_{\text{tot}}\rangle\right) + \sum_{i=2}^{k}\Delta\mu_i\left(\widetilde{N}_i - \langle N_i\rangle\right) \\ &\quad - \left(\widetilde{U} - \langle U\rangle\right). \end{aligned} \tag{22}$$

We point out that because we used Eq. (12) directly to simplify the derivatives of the partition functions, and this final expression is structurally identical regardless of whether kinetic energy contributions are included or neglected. This is because the form of Eq. (12) holds regardless; thus U is left ambiguous as Eq. (22) may be applied both when $U = U_{\text{p}}$ and when $U = U_{\text{tot}}$. Only for higher order terms does this distinction begin to matter.

B. Higher order terms

The next derivative of Eq. (22) at each value of N_{tot} is simply given by

$$\begin{aligned} \frac{\partial^2 \ln \Pi(N_{\text{tot}})}{\partial \beta^2} &= -\mu_1\frac{\partial\langle N_{\text{tot}}\rangle}{\partial \beta} + \sum_{i=2}^{k}\Delta\mu_i\left(\frac{\partial \widetilde{N}_i}{\partial \beta} - \frac{\partial\langle N_i\rangle}{\partial \beta}\right) \\ &\quad - \left(\frac{\partial \widetilde{U}}{\partial \beta} - \frac{\partial\langle U\rangle}{\partial \beta}\right). \end{aligned} \tag{23}$$

Rather than further simplifying this expression immediately, as has been done in previous work,[12] we leave this explicitly in terms of the first derivatives of extensive properties. The reason we do so is to illustrate that all second and higher order derivatives of $\ln \Pi(N_{\text{tot}})$ may be expressed in terms of moments that can be obtained from the $Z(N_{\text{tot}};\vec{\xi})$ matrix. We begin by considering the derivatives of isochoric semigrand ensemble-averaged extensive moments, $\widetilde{Z}$,

$$\begin{aligned}\frac{\partial \widetilde{Z}}{\partial \beta} &= \frac{\partial}{\partial \beta}\left[\frac{1}{\Upsilon}\sum_{N_2}\cdots\sum_{N_k} Z\exp\left(\beta\sum_{i=2}^{k}\Delta\mu_i N_i\right)Q\right]\\ &= \frac{1}{\Upsilon}\sum_{N_2}\cdots\sum_{N_k}\left(-ZU+\frac{\partial Z}{\partial\beta}+Z\sum_{i=2}^{k}\Delta\mu_i N_i\right)\exp\left(\beta\sum_{i=2}^{k}\Delta\mu_i N_i\right)Q-\frac{1}{\Upsilon}\frac{\partial\Upsilon}{\partial\beta}\frac{1}{\Upsilon}\sum_{N_2}\cdots\sum_{N_k} Z\exp\left(\beta\sum_{i=2}^{k}\Delta\mu_i N_i\right)Q\\ &= \sum_{i=2}^{k}\Delta\mu_i\tilde{f}\left(\widetilde{Z},\widetilde{N}_i\right)-\tilde{f}\left(\widetilde{Z},\widetilde{U}\right)+\widetilde{\frac{\partial Z}{\partial\beta}}.\end{aligned} \tag{24}$$

Here, $\tilde{f}(\widetilde{X},\widetilde{Y}) \equiv \widetilde{XY}-\widetilde{X}\widetilde{Y}$ is the fluctuation of quantities X and Y in the isochoric semigrand ensemble. Note the difference between $\widetilde{\frac{\partial Z}{\partial\beta}}$, which is the ensemble average of the derivative, and $\frac{\partial\widetilde{Z}}{\partial\beta}$, which is the derivative of the ensemble-averaged quantity $\widetilde{Z}$. When Z does not involve energy, e.g., for all $Z(N_{\text{tot}};\vec{\xi})$ where $\xi_{\text{u}}=0$, then $\widetilde{\frac{\partial Z}{\partial\beta}}=0$. More generally, in the case where we neglect kinetic contributions altogether, this final term and all its subsequent derivatives are always zero, regardless of ξ_{u}, since no term in the $Z(N_{\text{tot}};\vec{\xi})$ matrix depends on β; thus it may be removed from Eq. (24).[12]

However, if kinetic energy is included, then $U=U_{\text{tot}}$. Thus, the final term in Eq. (24) must be considered for all $Z(N_{\text{tot}};\vec{\xi})$ where $\xi_{\text{u}}>0$. In this case, for a system of monatomic particles, from Eq. (17) we have

$$\frac{\partial Z}{\partial\beta}=-\frac{d\xi_{\text{u}}}{2}\beta^{-2}N_{\text{tot}}RU_{\text{tot}}^{\xi_{\text{u}}-1}. \tag{25}$$

Note that for fluids composed of polyatomic molecules with internal degrees of freedom, the kinetic energy will depend on the number of degrees of freedom in the system, not just the total number of particles. Consequently, the above expression becomes slightly more involved and will further complicate total-energy extrapolation but does not affect the configurational extrapolation approach, for which $\widetilde{\frac{\partial Z}{\partial\beta}}=0$. Incorporating the ensemble average of this derivative into Eq. (24) we arrive at

$$\begin{aligned}\frac{\partial\widetilde{Z}}{\partial\beta} &= \sum_{i=2}^{k}\Delta\mu_i\tilde{f}\left(\widetilde{Z},\widetilde{N}_i\right)-\tilde{f}\left(\widetilde{Z},\widetilde{U}\right)+\\ &\quad -\frac{d\xi_{\text{u}}}{2}\beta^{-2}N_{\text{tot}}\widetilde{RU_{\text{tot}}^{\xi_{\text{u}}-1}}.\end{aligned} \tag{26}$$

Following a similar procedure in the grand canonical ensemble, we have

$$\begin{aligned}\frac{\partial\langle Z\rangle}{\partial\beta} &= \mu_1\hat{f}\left(\langle Z\rangle,\langle N_{\text{tot}}\rangle\right)+\sum_{i=2}^{k}\Delta\mu_i\hat{f}\left(\langle Z\rangle,\langle N_i\rangle\right)+\\ &\quad -\hat{f}\left(\langle Z\rangle,\langle U\rangle\right)+\left\langle\frac{\partial Z}{\partial\beta}\right\rangle\\ &= \mu_1\hat{f}\left(\langle Z\rangle,\langle N_{\text{tot}}\rangle\right)+\sum_{i=2}^{k}\Delta\mu_i\hat{f}\left(\langle Z\rangle,\langle N_i\rangle\right)+\\ &\quad -\hat{f}\left(\langle Z\rangle,\langle U\rangle\right)-\frac{d\xi_{\text{u}}}{2}\beta^{-2}\langle N_{\text{tot}}RU_{\text{tot}}^{\xi_{\text{u}}-1}\rangle,\end{aligned} \tag{27}$$

where $\hat{f}(\langle X\rangle,\langle Y\rangle)\equiv\langle XY\rangle-\langle X\rangle\langle Y\rangle$ is the fluctuation of quantities X and Y in the grand canonical ensemble. We emphasize that the final term in both Eqs. (26) and (27) is not present when kinetic effects are neglected (configurational extrapolation). This is why the term "U" is left ambiguous in all but the final term in these equations, which arises solely from kinetic considerations, and thus is explicitly represented by U_{tot} to emphasize this point. For comparison, the reader may refer to Ref. 12 wherein kinetic effects have been neglected.

When the kinetic contributions are neglected, higher order derivatives of $Z(N_{\text{tot}};\vec{\xi})$ [and therefore $\ln\Pi(N_{\text{tot}})$] may be calculated recursively with the expressions given above by exploiting the fact that

$$\frac{\partial\tilde{f}(\widetilde{X},\widetilde{Y})}{\partial\beta}=\frac{\partial\widetilde{XY}}{\partial\beta}-\widetilde{X}\frac{\partial\widetilde{Y}}{\partial\beta}-\widetilde{Y}\frac{\partial\widetilde{X}}{\partial\beta}. \tag{28}$$

A similar expression holds for $\hat{f}(\langle X\rangle,\langle Y\rangle)$.[12] Higher order derivatives of $\ln\Pi(N_{\text{tot}})$ clearly involve taking higher order derivatives of Eqs. (26) and (27), e.g., $\partial^3\ln\Pi(N_{\text{tot}})/\partial\beta^3$ requires $\partial^2\widetilde{Z}/\partial\beta^2$ and $\partial^2\langle Z\rangle/\partial\beta^2$. Through the repeated use of Eq. (28) in Eq. (26), and its grand canonical analog in Eq. (27), one may calculate all higher order derivatives of Eq. (23); therefore, expressions for the coefficients in Eq. (14) are known up to arbitrary order since Eqs. (26) and (27) only involve fluctuation quantities. Note that all necessary quantities X and Y are terms found in the $Z(N_{\text{tot}};\vec{\xi})$ matrix, which enables this calculation.

When kinetic contributions are taken into account, the trailing "corrections" due to $\widetilde{\frac{\partial Z}{\partial \beta}}$ and $\langle \frac{\partial Z}{\partial \beta} \rangle$ in Eqs. (26) and (27), respectively, are generally non-zero. As a result, the expressions for the derivatives do not exclusively involve fluctuations. Equation (28) may again be used to compute the derivatives of fluctuations when necessary, but derivatives of these trailing terms must also be computed. While this is not difficult, it is more tedious and involved. For example, second derivatives of terms in the $Z(N_{\text{tot}};\vec{\xi})$ matrix may be expressed as

$$\frac{\partial^2 \widetilde{Z}}{\partial \beta^2} = \sum_{i=2}^{k} \Delta\mu_i \frac{\partial \tilde{f}(\widetilde{Z},\widetilde{N}_i)}{\partial \beta} - \frac{\partial \tilde{f}(\widetilde{Z},\widetilde{U})}{\partial \beta} - \frac{d\xi_{\text{u}}}{2}\beta^{-2} N_{\text{tot}} \left(-2\beta^{-1} \widetilde{RU_{\text{tot}}^{\xi_{\text{u}}-1}} + \frac{\partial \widetilde{RU_{\text{tot}}^{\xi_{\text{u}}-1}}}{\partial \beta} \right), \tag{29}$$

$$\frac{\partial^2 \langle Z \rangle}{\partial \beta^2} = \mu_1 \frac{\partial \hat{f}(\langle Z \rangle, \langle N_{\text{tot}} \rangle)}{\partial \beta} + \sum_{i=2}^{k} \Delta\mu_i \frac{\partial \hat{f}(\langle Z \rangle, \langle N_i \rangle)}{\partial \beta} - \frac{\partial \hat{f}(\langle Z \rangle, \langle U \rangle)}{\partial \beta} + \\ - \frac{d\xi_{\text{u}}}{2}\beta^{-2} \left(-2\beta^{-1} \langle N_{\text{tot}} RU_{\text{tot}}^{\xi_{\text{u}}-1} \rangle + \frac{\partial \langle N_{\text{tot}} RU_{\text{tot}}^{\xi_{\text{u}}-1} \rangle}{\partial \beta} \right). \tag{30}$$

Again, the trailing terms in parentheses are not present when kinetic effects are ignored. Although Eqs. (26) and (27) may be applied again to terms in these equations to compute higher order derivatives of these expressions, the prefactor of β^{-2} implies that the chain rule must be applied each time an additional derivative is taken, significantly increasing the length and complexity of the resulting expressions. Nonetheless, all the tools necessary to obtain expressions for higher order derivatives have now been provided. We simply remark that when kinetic contributions are ignored, the derivatives retain a significantly more compact mathematical form, and as we will now illustrate, also tend to produce more accurate extrapolations.

IV. COMPARING THE TWO APPROACHES

A. Consistency with the acceptance criterion

For a system in which kinetic contributions have been included, the (unbiased) Metropolis acceptance criterion is different from the case when it is not. The energy that is recorded in the $Z(N_{\text{tot}};\vec{\xi})$ matrix must be consistent with this choice. In both instances, the probability of accepting a proposed Monte Carlo move from one microstate to another, "x" → "y," is given by

$$p_{\text{acc}} = \min\left[1, \frac{\pi(y)}{\pi(x)}\right], \tag{31}$$

where $\pi(s)$ is the probability of observing microstate "s." Clearly this depends on the choice of Q. In TMMC, p_{acc} is directly used to construct the macrostate distribution. Therefore, $\ln \Pi(N_{\text{tot}})$ and its derivatives depend on the choice of whether to include kinetic energy effects. When kinetic contributions have been incorporated

$$\pi_{\text{k}}(s) = \frac{\exp\left(-\beta U_{\text{p}}\right)}{\Xi} \prod_{i=1}^{k} \frac{V^{N_i(s)} \exp\left(\beta \mu_i N_i(s)\right)}{\Lambda_i^{dN_i(s)} N_i(s)!}, \tag{32}$$

whereas when they have been neglected, the de Broglie wavelength terms are absent from the denominator [$\pi_{\text{p}}(s) = \pi_{\text{k}}(s)/Q_{\text{k}}(s)$]. If one uses Eq. (32) as written, then the energy elements of the $Z(N_{\text{tot}};\vec{\xi})$ matrix must explicitly include kinetic energy ($U = U_{\text{tot}}$) to perform total-energy extrapolation. Note that neglecting the kinetic energy is more consistent with the fact that Monte Carlo inherently only samples the configurational contribution to the partition function (or the configurational integral) and thus focuses on potential energy. In the case where kinetic effects are neglected from the system's partition function (configurational extrapolation), the de Broglie wavelength terms should be removed from the acceptance criterion, and only the potential energy should contribute to the energy terms in the $Z(N_{\text{tot}};\vec{\xi})$ matrix ($U = U_{\text{p}}$).

At fixed temperature, the difference between the forms of Eq. (32) is actually subtle and essentially irrelevant as the two are equivalent if one incorporates the factor of $\Lambda_i^{dN_i(s)}$ into the chemical potential of species i,

$$\mu_{i,\text{eff}} = \mu_i - \overbrace{dk_{\text{B}}T \ln \Lambda_i}^{\mu_{i,\text{ref}}(\beta)}. \tag{33}$$

In this case, the effective chemical potentials are now simply a function of temperature. A similar procedure can be used to recast both the chemical potentials and kinetic portion of the canonical partition function into a single temperature-dependent activity instead, which can be specified as input to a GCMC simulation.[2,16–20] This choice is highly relevant when performing temperature extrapolation as the reference state for each component, $\mu_{i,\text{ref}}(\beta)$, now depends on temperature.

These approaches for implicitly incorporating Q_{k} by using an effective or relative chemical potential are common practice. Similarly, it is also common practice to only collect potential energy over the course of the simulation. Therefore, this represents the intermediate case where $Q = Q_{\text{tot}}$ but

$U = U_p$. As discussed in Sec. II C, it is critical to maintain consistency between the energy terms in the $Z(N_{tot}; \vec{\xi})$ matrix and the canonical partition function of the system in order to correctly evaluate the thermodynamic derivatives. These approaches still amount to requiring total-energy extrapolation, unless Λ_i is arbitrarily set to a constant value (such as unity) for all temperatures so that it is independent of β. In that case, kinetic effects have effectively been removed from the system's partition function and configurational extrapolation may be employed. This is the tactic we commonly adopt as it is always possible to simply shift the chemical potential, accounting for its reference state, after the relevant extrapolation or calculations have been performed. A detailed example calculation is provided in the Appendix for the interested reader.

B. Single-component, monatomic ideal gas

We generally find that more accurate extrapolations are obtained for fluid systems when kinetic effects are neglected. The interested reader may find detailed examples of various types of systems we have previously studied in Ref. 12. For the sake of brevity, and since the mathematics is particularly transparent, we focus here on the limiting case of a pure, monatomic ideal gas to illustrate why configurational extrapolation tends to be more accurate than total-energy extrapolation. Namely, for the pure ideal gas fluid, configurational extrapolation is "exact" at first order, and all higher order terms are identically zero, whereas when kinetic effects are incorporated, total-energy extrapolation is only exact if an infinite number of higher-order terms are included, becoming only an approximation when truncated to finite order. Therefore, a finite amount of error will always persist in the latter case, which we shall now prove.

As previously discussed, the form of Eq. (22) is independent of whether U_{tot} or U_p is used. Note that if we elected to perform total-energy extrapolation such that $U = U_{tot}$, Eq. (22) could be rewritten as

$$\frac{\partial \ln \Pi(N_{tot})}{\partial \beta} = \left(\mu_1 - \frac{d}{2}k_B T\right)(N_{tot} - \langle N_{tot}\rangle) + \sum_{i=2}^{k} \Delta\mu_i \left(\widetilde{N_i} - \langle N_i\rangle\right) - \left(\widetilde{U_p} - \langle U_p\rangle\right). \quad (34)$$

Thus, there is no structural change to the mathematical form of the derivative; it is only "evaluated" at a different effective chemical potential of species 1 that has been reduced by a factor originating from the inclusion of kinetic effects [cf. first term in parentheses on the right hand side of Eq. (34)].

However, since the moments in the $Z(N_{tot}; \vec{\xi})$ matrix depend on the choice of U, Eqs. (26) and (27) also depend on this choice, which in turn affect the second derivative of $\ln \Pi(N_{tot})$, Eq. (23). From Eqs. (26) and (27), the reader will observe that to second order, a factor of $\frac{d}{2}\beta^{-2}(N_{tot} - \langle N_{tot}\rangle)$ appears during the evaluation of Eq. (23) when kinetic effects are included, while it is absent otherwise. As already discussed, higher order expansions of $\ln \Pi(N_{tot})$ with kinetic effects included deviate by progressively more complicated mathematical expressions because of chain rules that must be applied to take additional derivatives of this term.

Notably, in the special case of a single-component ideal gas, significant simplifications may be made. If we neglect kinetic contributions, we may express the macrostate distribution as

$$\ln \Pi(N; \beta) = \ln \Pi(N; \beta^0) + \mu(N - \langle N\rangle)\Delta\beta + \frac{1}{2}(0)\,\Delta\beta^2 + \ldots. \quad (35)$$

Since $U = U_p = 0$ for an ideal gas, second order and higher terms are identically zero in Eq. (14), and thus the Taylor series expansion is actually "exact" at first order.

The same is not true when kinetic contributions are included because $U = U_k + U_p = U_k = \frac{d}{2}N\beta^{-1} \neq 0$. Using this relationship, Eq. (14) may be simplified in terms of only the particle number. For a three-dimensional ideal gas, up to second order, in the thermodynamic limit,

$$\ln \Pi(N; \beta) = \ln \Pi(N; \beta^0) + \left(\mu - \frac{3}{2}\beta^{-1}\right)(N - \langle N\rangle)\,\Delta\beta + \frac{1}{2}\left(\frac{3}{2}\beta^{-2}(N - \langle N\rangle) - \left(\mu - \frac{3}{2}\beta^{-1}\right)^2 \hat{f}(\langle N\rangle, \langle N\rangle)\right)\Delta\beta^2. \quad (36)$$

However, this expansion is no longer exact, and higher order terms are non-zero. This illustrates why there are accuracy differences between configurational and total-energy extrapolation.

To quantitatively compare the two cases, we simulated a three-dimensional ideal gas at several temperatures when kinetic contributions were included and when they were neglected. To construct the equation of state ($\rho = N/V$ vs. P diagram) at lower temperature (higher β), first $\ln \Pi(N; \beta^0)$ was reweighted to a desired μ and then extrapolated from β^0 to β. When kinetic effects are neglected, the expression for temperature extrapolation is exact when truncated to first order. Indeed, to within nearly machine precision, our extrapolations agreed precisely with direct simulations at lower temperature and with the ideal gas equation of state. The ideal gas chemical potential and density are related by

$$\mu - \mu_{ref} = k_B T \ln\langle\rho\rangle, \quad (37)$$

where, according to our convention, $\mu_{ref} = 0$ when kinetic contributions are neglected. However, when kinetic contributions are present $\mu_{ref} = 3k_B T \ln \Lambda$ [cf. Eq. (33)], which is a function of temperature.

Consequently, when kinetic effects are incorporated, total-energy extrapolation to different temperatures at a fixed value of μ means that the quantity $\mu - \mu_{ref}$ (related to the activity) changes. In general, to make a comparison at identical state points, one must take care with respect to the reference state of the system. Henceforth, we report $\mu - \mu_{ref}$ to emphasize a fair

comparison at "identical" conditions. This is important when comparing simulations that did incorporate kinetic effects to those that did not.

In Fig. 1(a), we report the equation of state obtained from total-energy extrapolation from $k_BT = 1.35$ to $k_BT = 1.05$, 0.85 ($\Delta\beta = 0.21, 0.44$, respectively). Remarkably, we recovered ρ vs. P curves that were nearly identical to those obtained by direct simulation at lower temperature (same as the equation of state), regardless of the order of extrapolation. This is unusual since the Taylor series expansion is only approximate in this case. However, upon closer inspection, it is apparent that the chemical potential at each point in the parameterized ρ vs. P state space depends on the order of extrapolation, even if the change in reference state is accounted for correctly.

Figure 1(b) shows a comparison between different orders of extrapolation for different $\Delta\beta$ values. Note that the first and second order predictions "oscillate" around the analytic ideal gas equation of state [black curves, Eq. (37)] at the lower temperature, progressively converging as the order increases. Furthermore, the deviation between this equation of state and extrapolated simulations increases in magnitude with larger $\Delta\beta$. Plots of density versus chemical potential reveal a similar oscillation. The result is that when plotted parametrically, the extrapolated pressure versus density points appear to still fall along the line determined by the known equation of state; however, they appear to be shifted along that line relative to the true ideal gas equation. If low temperature results from $k_BT = 0.85$ are extrapolated to high temperatures ($k_BT = 1.05$, 1.35), the predictions converge to the equation of state in an asymptotic manner from one side only, rather than alternating about the exact result [cf. Fig. 1(c)]. The reason for the different behavior will be subsequently discussed in detail in Sec. IV C. Regardless, here we reiterate the contrast between this inexact, but converging, behavior with that of configurational extrapolation, which produces an exact result at different values of β.

In spite of the erroneous prediction of the chemical potential corresponding to a given point in ρ vs. P state space, it is curious to see that the correct parameterization (equation of state) seems to be recovered nonetheless. The reason is linked to the observation that the difference between the extrapolated macrostate distribution and that obtained from direct simulation, $\delta\ln[\Pi(N)/\Pi(0)]_{\text{ext}-\text{sim}}$, is essentially linear with N regardless of the value of μ [cf. Fig. 1(d)]. Recall that prior to temperature extrapolation, a given macrostate distribution is first reweighted to some desired μ using Eq. (5). When using this equation to exactly reweight a distribution from one μ to another at a fixed β, a linear shift in the slope of $\ln\Pi(N)$ vs. N is the result of simply adjusting the value of $\mu \to \mu + \delta\mu$. This means that the difference between $\ln\Pi(N)$ distributions obtained from direct simulation at β, and extrapolation from β^0 to β, may be largely "masked" by artificially using a slightly different μ value in each case to "correct" for deviations resulting from truncation of the extrapolated macrostate distribution.

Consequently, the extrapolated results appear to correspond to a different value of μ when compared to direct simulations (equivalent to the known equation of state). This artificial adjustment is clearly a function of the order of extrapolation used since the Taylor series expansion is inexact when kinetic effects are included, and the error will depend on the

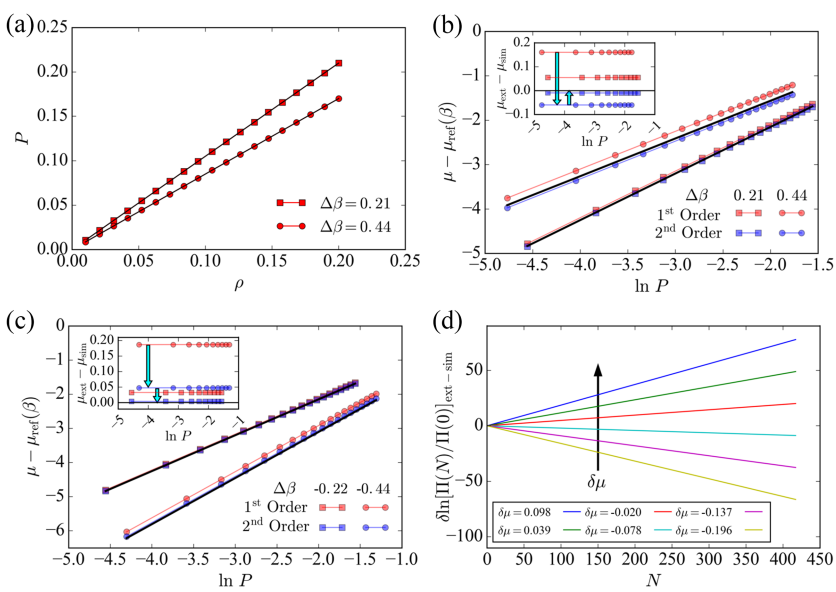

FIG. 1. Comparing total-energy extrapolation to direct simulation for a single-component ideal gas. Pressure, P, is reported in units of k_BT/V. (a) Results from the equation of state (black lines) and extrapolation from $k_BT = 1.35$ to two lower temperatures ($k_BT = 1.05$, 0.85 such that $\Delta\beta = 0.21, 0.44$, respectively). First and second order extrapolations are visually indistinguishable, so only the first order results are shown for clarity. (b) Comparison between the ideal gas equation of state (black lines) and the chemical potential that the points in (a) were obtained at. The inset shows the difference between the chemical potentials corresponding to the extrapolated and direct simulations (identical to equation of state) for different orders of extrapolation. (c) Comparison between extrapolation and direct simulation as in (b), where instead the simulations performed at $k_BT = 0.85$ were extrapolated to higher temperatures ($k_BT = 1.05$, 1.35). (d) Difference between the simulated macrostate distribution at $k_BT = 0.85$ where $\mu_{\text{sim}} \approx -1.96$ and ones reweighted to slightly different chemical potentials, $\delta\mu = \mu_{\text{ext}} - \mu_{\text{sim}}$, when extrapolated from $k_BT = 1.35$ ($\Delta\beta = 0.44$) using second order corrections.

number of terms chosen. This approximately linear deviation between extrapolated and directly simulated macrostate distributions (which incorporate kinetic effects) seems to generally occur for other systems as well, including binary systems, such as those in Ref. 12, and the pure component square-well fluid discussed in Sec. IV D. The noteworthy consequence of this fortuitous "cancellation of errors" is that the equation of state [parameterization of the observable properties, e.g., $\rho(\mu, \beta)$ vs. $P(\mu, \beta)$] for a fluid may be very nearly obtained correctly even with the extrapolated $\ln \Pi(N_{\text{tot}})$ when kinetic effects are included (total-energy extrapolation). The only caveat is that the chemical potential predicted by extrapolation at a given state point is not as accurate in this case. However, this is often perfectly acceptable as the chemical potential is not a quantity of concern; it is the observable properties predicted by the parameterized equation of state that are important.

C. Underlying source of the accuracy difference

The source of the "oscillations" in the value of the chemical potentials when using total-energy extrapolation to examine lower temperature states may be traced directly back to the trailing "correction" due to $\widetilde{\frac{\partial U_{\text{tot}}}{\partial \beta}}$ in Eq. (26). To understand this, we point out that grand canonical ensemble-averaged quantities may be actually neglected from these extrapolation expressions entirely. This potentially surprising assertion arises from the fact that these terms, computed via Eq. (6), are constant across all values of the order parameter. Consequently, they serve only to multiply the macrostate probabilities by some constant value, or, in log-space, to shift $\ln \Pi(N_{\text{tot}})$ by some fixed value as a result of extrapolation. These shifts have no effect on the properties computed from the resulting macrostate distribution [cf. Eq. (6) or Eq. (7), for example] and are akin to simply changing the reference state of the system. In other words, Eq. (22) could be expressed instead as

$$\frac{\partial \ln \Pi(N_{\text{tot}})}{\partial \beta} = \mu_1 N_{\text{tot}} + \sum_{i=2}^{k} \Delta\mu_i \widetilde{N_i} - \widetilde{U_{\text{tot}}} + C, \tag{38}$$

where C is some constant that may be disregarded in practice.

Furthermore, the macrostate probability distribution is generally normalized before it is used in any computation, which essentially nullifies the significance of the value of C. In light of this, we may reconsider the extrapolation equations in terms of only their semigrand contributions to investigate the source of the difference between total-energy and configurational extrapolation. This means that the difference between the methods is not a consequence of the trailing correction from $\langle \frac{\partial Z}{\partial \beta} \rangle$ in Eq. (27) but is solely a result of the terms originating from $\widetilde{\frac{\partial Z}{\partial \beta}}$ in Eq. (26).

If we consider the specific case of a single-component, monatomic ideal gas, we may express the first derivative of the macrostate distribution as follows:

$$\frac{\partial \ln \Pi}{\partial \beta} \sim \mu N - \widetilde{U_{\text{tot}}} = N\left(\mu - \frac{d}{2}\beta^{-1}\right). \tag{39}$$

Note that the sign of this term is ambiguous and depends on the relative magnitude of the chemical potential with respect to β. The reader will note then that the sign of subsequent derivatives will alternate due to the negative exponent on β. For example, consistent with the above expression, Eq. (26) becomes

$$\frac{\partial^2 \ln \Pi}{\partial \beta^2} \sim -\frac{\partial \widetilde{U_{\text{tot}}}}{\partial \beta} = \cancel{\tilde{f}\left(\widetilde{U_{\text{tot}}}, \widetilde{U_{\text{tot}}}\right)} - \frac{\partial \widetilde{U_{\text{tot}}}}{\partial \beta} = \frac{d}{2}\beta^{-2}N > 0. \tag{40}$$

In this case, $U_{\text{tot}} = \cancel{U_{\text{p}}} + U_{\text{k}} = 3Nk_{\text{B}}T/2$ in the thermodynamic limit, so $\tilde{f}\left(\widetilde{U_{\text{tot}}}, \widetilde{U_{\text{tot}}}\right) = 0$ at fixed N. The third order derivative is then

$$\frac{\partial^3 \ln \Pi}{\partial \beta^3} \sim -2\frac{d}{2}\beta^{-3}N < 0, \tag{41}$$

and so on. Thus, excepting the first order derivative whose sign is ambiguous, coefficients on the odd powers in the Taylor series are negative, and coefficients on even powers are positive.

Now consider the case when simulations are extrapolated to lower temperatures, $\Delta\beta = 1/(k_{\text{B}}T_{\text{final}}) - 1/(k_{\text{B}}T_{\text{initial}}) > 0$. It follows that $(\Delta\beta)^n$ is non-negative for all n, and thus, the sign of each term in the Taylor series is determined by the sign of the coefficient. Since the sign of the coefficients alternate, as shown above, the net result is that the sign of the terms in the Taylor series also alternates. Combined with the "masking" of errors discussed in the Sec. IV B, the chemical potential that seems to correspond to a point in phase space responds in a complementary way. For instance, if the macrostate is underestimated by the truncated extrapolation, the chemical potential that would appear to correspond to a given state point will be overestimated in an attempt to compensate for this error [cf. Fig. 1(b)].

In contrast, when extrapolating simulation data to higher temperatures, $\Delta\beta < 0$. Now the quantity $(\Delta\beta)^n > 0$ for even values of n, whereas $(\Delta\beta)^n < 0$ odd values of n. However, because the coefficients on odd (even) order terms are also negative (positive), all terms in this Taylor series will be positive. Therefore truncation of the series always leads to a Taylor polynomial, which underestimates the correct macrostate distribution, leading to an overestimation of the chemical potential corresponding to that state [cf. Fig. 1(c)].

Note that when extrapolating the moment matrix, $Z(N_{\text{tot}}; \vec{\xi})$, a similar issue will arise. This extrapolation must be done in addition to that of the macrostate distribution in multicomponent systems to evaluate properties such as mole fractions via Eq. (6).[12] Although we cannot make the same logical simplification for more complex (non-ideal, multicomponent) systems, we suggest that similar behavior may manifest in other cases, especially where the system is only weakly non-ideal. We again emphasize that regardless of the nature of the deviation from direct simulations, either oscillating or asymptotically approaching, this behavior stands in stark contrast to the case of configurational extrapolation that represents an exact result in this particular case.

Ultimately, it is not simply an issue of incorrect reference states, or poor convergence of simulations. The reason that total-energy extrapolation tends to be less accurate than configurational extrapolation is that the former requires the inclusion of more terms in its Taylor series expansion to converge to the correct macrostate distribution at a given set of external conditions. This is primarily a consequence of the fact that $U = U_{\text{tot}}$, which is not independent of β, and thus the trailing $\widetilde{\frac{\partial U}{\partial \beta}}$ term in Eq. (26), which must be computed to evaluate Eq. (23), is non-zero. This amplifies each term in the Taylor series from second order and beyond, implying that truncation at a finite order leads to greater error than in the case of configurational extrapolation.

D. Subcritical square-well fluid

The superior accuracy of configurational extrapolation over total-energy extrapolation is mathematically straightforward to realize in the case of an ideal gas since particle-energy correlations are identically zero, allowing us to greatly simplify Eq. (14). However, more realistic, non-ideal systems do not have such simple particle-energy correlations. While it is not immediately obvious that the same conclusion should hold, extrapolation results for the systems we have studied thus far suggest that this is the case.

As an example of this, here we have computed the saturation properties of the subcritical square-well fluid described in Sec. II D. We performed direct simulations at $k_{\text{B}}T/\epsilon_{1,1} = T^* = 1.35, 1.20, 1.15, 1.10$, and 1.05 when kinetic effects were included and when they were neglected. Four independent replicates were performed to obtain statistical averages. The critical temperature for this fluid is $T_c^* \approx 1.22$,[7] and we extrapolated the supercritical results to subcritical temperatures for comparison. The results of second order extrapolation are depicted in Fig. 2.

Regardless of whether kinetic effects were included, the saturation properties were found to be within simulation uncertainty of each other (standard error less of than 1%). This holds true even when comparing to results obtained from extrapolation instead of direct simulation [cf. Fig. 2(a)]. In other words, once again, essentially the same equation of state is recovered in both instances. However, as in the case of an ideal gas, when kinetic effects were included, the chemical potential at which coexistence was predicted via extrapolation deviated systematically from direct simulations [cf. Figs. 2(b) and 2(c)]. In contrast, the following yielded statistically identical saturation properties: direct simulations including kinetic contributions, direct simulations ignoring kinetic contributions, and configurational extrapolation. The macrostate distribution at coexistence for all these cases is given in Fig. 2(d). Simulations with and without kinetic effects present are visually identical, again deviating by at most 1% from each other, as are the distributions obtained from extrapolation of each case. It is clear in both instances that the extrapolated results deviate systematically from those obtained from direct simulation, as previously noted in Ref. 12.

However, even when the reference state is properly accounted for in total-energy extrapolation, the chemical potential that yields the extrapolated distribution deviates systematically from that of the fluid's "true" equation of state. In other words, the results of extrapolation with and without kinetic contributions are essentially identical at coexistence in Fig. 2(d) (blue and black, respectively). However, these $\ln \Pi(N)$ distributions were obtained at slightly different chemical potentials [cf. Fig. 2(c)]. In contrast, for configurational extrapolation, the chemical potential corresponding to the extrapolated macrostate distribution is in agreement with that obtained from direct simulation neglecting kinetic effects.

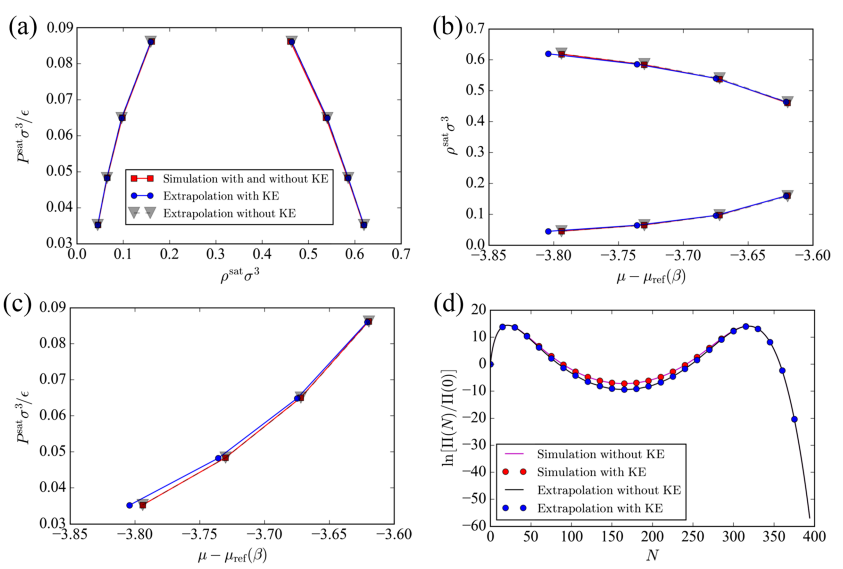

FIG. 2. Comparison between second order extrapolation and direct simulation for the square-well fluid discussed in the text. Simulations were performed at $T^* = 1.35$ and extrapolated to $T^* = 1.20, 1.15, 1.10$, and 1.05. Results were averaged over 4 independent replicates and standard errors are smaller than symbol size. (a) Saturation properties obtained from direct simulation and extrapolation. Direct simulation results when kinetic effects were neglected are visually identical to those obtained when they are accounted for (red) and so are not shown for clarity. (b) Saturation density vs. chemical potential for the cases in (a), with corresponding symbols. (c) Saturation pressure vs. chemical potential for the cases in (a), with corresponding symbols. (d) Macrostate distributions at coexistence for $T^* = 1.05$.

V. CONCLUSIONS

We have derived a method for extrapolating the macrostate distribution obtained via flat-histogram multicomponent grand canonical Monte Carlo simulations from one temperature to another. The derivation presented here is generalized to include the case when kinetic energy contributions are explicitly included in the system's partition function (total-energy extrapolation). Generally speaking, the inclusion of kinetic effects has a number of disadvantages over the case when they are factored out of the system's canonical partition function *a priori* and neglected (as in configurational extrapolation). First, the reference state of the fluid changes when extrapolating $\ln \Pi(N_{\text{tot}})$ to different temperatures. Although this is not too cumbersome to handle appropriately, it is a complication that may be avoided by simply disregarding the kinetic effects to begin with. Furthermore, even when changes in the reference state(s) are appropriately treated, the Taylor series expansion of the macrostate distribution tends to converge more slowly when kinetic effects are included than when they are neglected. Intuitively, one may attribute this to the additional terms in each coefficient (derivative) of the Taylor series, which are required to account for the temperature dependence of the kinetic energy. As a result, the magnitude of the coefficients tends to be larger, and thus a greater error is introduced upon truncation to finite order.

In the limiting case of a single-component ideal gas, a first order expansion is actually exact when kinetic effects are neglected, while it is only approximate when kinetic effects are included. As a result, truncation beyond first order introduces no error in the former but always a finite amount in the latter. However, due to the nature of the Taylor series expansion, this error may be masked by shifting the chemical potential, beyond just adjusting the reference state appropriately. Consequently, it appears that the observable properties of many fluids may still be parameterized accurately by the total-energy extrapolation method, though the chemical potential corresponding to a given thermodynamic state will contain some amount of error that depends on the order of the expansion. This error tends to be significantly smaller, often less than simulation uncertainty, in configurational extrapolation where kinetic effects are disregarded.

In conclusion, as it is generally not necessary to account for kinetic effects during Monte Carlo simulations (a change in reference states may be handled after the fact), we do not recommend incorporating them when implementing our method. However, when this is unavoidable, e.g., in the case where such data are already available or these effects must be included for other purposes, the method we have presented here may be employed to predict $\ln \Pi(N_{\text{tot}})$ at a desired temperature from simulations performed at a different one.

ACKNOWLEDGMENTS

N.A.M. gratefully acknowledges support from a National Research Council postdoctoral research associateship at the National Institute of Standards and Technology. N.A.M. would also like to thank Daniel W. Siderius for fruitful discussions and for pointing out simplifications in the methodology. J.R.E. acknowledges support from the National Science Foundation, Grant No. CHE-1362572.

APPENDIX: EXAMPLE CALCULATION

Here we provide a step-by-step example of how to apply our extrapolation procedure to data obtained from a flat-histogram grand canonical Monte Carlo simulation. We explicitly illustrate this for the square-well system we reported in Sec. IV D at saturation conditions. Depicted in Fig. 3 are the three stages involved in this procedure. Here we have performed a simulation in which kinetic effects were explicitly accounted for and where we set $\mu = -5$. First, we reweight the macrostate distribution from $\mu = -5$ to $\mu \approx -3.949$ at a fixed value of $\beta = 1/1.35$ ($1 \rightarrow 2$) using Eq. (5). Note that the reference state of the fluid is irrelevant here because we are subtracting two chemical potentials at the same temperature, which causes these terms to cancel out. Subsequently, we extrapolate in temperature to a final state of $\beta = 1/1.20$ ($2 \rightarrow 3$) using the equations given in Sec. III up to second order. The net result corresponds to the extrapolation estimate of saturation conditions at $T^* = 1.20$, which are essentially identical to direct simulations in this particular case (cf. Fig. 2).

Since the reference state of the fluid changes throughout this procedure, we explicitly detail the value of the activity, $z = \exp(\beta\mu)\,\Lambda^{-3}$, at each stage in Table I. For this example, we explicitly took $m = h^2/(2\pi)$ such that $\Lambda = \sqrt{\beta}$. When simulations are performed at $T^* = 1.20$ where kinetic effects are not accounted for (i.e., effectively setting $\Lambda = 1$ so that $\mu_{\text{ref}} = 0$), then the saturation point corresponds to $\mu_{\text{eff}} = \mu - \mu_{\text{ref}} = \mu \approx -3.621$. Indeed, when kinetic effects are accounted for, $\mu_{\text{eff}} \approx -3.621$ also corresponds to saturation, except now $\mu \approx -3.949$, since $\mu_{\text{ref}} = 3 * 1.20 * \ln\sqrt{1/1.20} \approx -0.328$. Note that $\beta\mu_{\text{eff}} = \ln z$. It is worth reiterating that in the case where kinetic effects are neglected, $\mu_{\text{eff}} = \mu$, which does not change from $2 \rightarrow 3$, whereas when the effects are included, μ is constant while μ_{eff} is not.

Here, we chose to first reweight and then extrapolate the distribution. However, the order may be reversed. Consider a

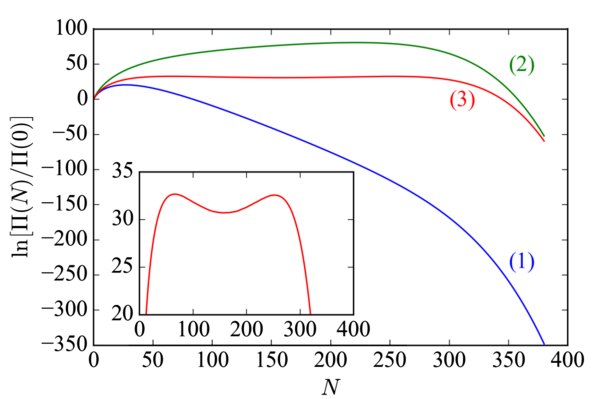

FIG. 3. Reweighting ($1 \rightarrow 2$) and subsequent extrapolation ($2 \rightarrow 3$) of the macrostate distribution from $T^* = 1.35$ to saturation conditions at $T^* = 1.20$ for the square-well fluid considered in Sec. IV D when kinetic effects have been accounted for. The exact conditions of each curve are reported in Table I.

TABLE I. Conditions corresponding to each stage in the manipulation of $\ln \Pi(N)$ depicted in Fig. 3 originally obtained at $T^* = 1.35$ for the square-well fluid studied in Sec. IV D. In this simulation, kinetic effects have been accounted for explicitly.

	(1)	(2)	(3)
β	1/1.35	1/1.35	1/1.20
μ	−5	−3.949	−3.949
$\ln z$	−3.254	−2.475	−3.017
μ_{eff}	−4.392	−3.341	−3.621

pure component system that is first reweighted from (β^0, μ^0) to (β^0, μ^f) then extrapolated to (β^f, μ^f); in that case, neglecting the grand canonical quantities as described in Sec. IV C, the final macrostate distribution may be expressed as

$$\begin{aligned}\ln \Pi(N; \beta^f, \mu^f) &\sim \overbrace{\left[\ln \Pi(N; \beta^0, \mu^0) + \beta^0 \left(\mu^f - \mu^0\right) N\right]}^{\text{Reweighting}} \\ &\quad + \overbrace{\left(\mu^f N - \widetilde{U}\right) \Delta\beta + \cdots}^{\text{Extrapolation}} \\ &= \ln \Pi(N; \beta^0, \mu^0) + \left(\beta^f \mu^f - \beta^0 \mu^0\right) N \\ &\quad - (\beta^f - \beta^0)\widetilde{U} + \cdots . \end{aligned} \tag{A1}$$

Here, we have only written the expression up to first order since higher orders are independent of the value of μ. Similarly, if one first extrapolates from (β^0, μ^0) to (β^f, μ^0) and then reweights to (β^f, μ^f), we obtain an identical expression

$$\begin{aligned}\ln \Pi(N; \beta^f, \mu^f) &\sim \overbrace{\left[\ln \Pi(N; \beta^0, \mu^0) + \left(\mu^0 N - \widetilde{U}\right) \Delta\beta + \cdots\right]}^{\text{Extrapolation}} \\ &\quad + \overbrace{\beta^f \left(\mu^f - \mu^0\right) N}^{\text{Reweighting}} \\ &= \ln \Pi(N; \beta^0, \mu^0) + \left(\beta^f \mu^f - \beta^0 \mu^0\right) N \\ &\quad - (\beta^f - \beta^0)\widetilde{U} + \cdots . \end{aligned} \tag{A2}$$

However, although the order of extrapolation and reweighting may be reversed, we suggest that it is better practice to perform the extrapolation as the last step in any manipulation. This is intuitive since reweighting is "exact," whereas extrapolation inevitably introduces some finite amount of error.

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