Estimating metastable thermodynamic properties by isochoric extrapolation from stable states

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The description of metastable fluids, those in a local but not global equilibrium, remains an important problem of thermodynamics and it is crucial for many industrial applications and all first order phase transitions. One way to estimate their properties is by extrapolation from nearby stable states. This is often done isothermally, in terms of a virial expansion for gases, or a Taylor expansion in density for liquids. This work presents evidence that an isochoric expansion of pressure in temperature is superior to an isothermal density expansion. Two different isochoric extrapolation strategies are evaluated, one best suited for vapors and one for liquids. Both are exact for important model systems, including the van der Waals equation of state. Moreover, we present a simple method to evaluate all the coefficients of the isochoric expansion directly from a simulation in the canonical ensemble. Using only properties of stable states, the isochoric extrapolation methods reproduce simulation results with Lennard-Jones potentials mostly within their uncertainties. The isochoric extrapolation methods are able to predict deeply metastable pressures accurately even from temperatures well above the critical. Isochoric extrapolation also predicts a mechanical stability limit, i.e. the thermodynamic spinodal. For water, the liquid spinodal pressure is predicted to be monotonically decreasing with decreasing temperature, in contrast to the re-entrant behavior predicted by the direct extension of the reference equation of state.

I. INTRODUCTION

Metastable fluids,[1] residing in a state of temporary equilibrium before transitioning to a more stable phase, stand as an intriguing topic of research in the area of thermodynamics. Examples include supersaturated steam, namely water vapor at a pressure above the dew pressure,[2,3] and supercooled water, which is liquid water at a temperature below the freezing point.[4] The concept of metastability is fundamental in the context of nucleation and phase transitions,[5,6] and to understand diverse phenomena such as transport of sap in trees,[7] the persistence of supercooled cloud droplets,[8] or the behavior of fluids in mineral inclusions, which represents a crucial tool to determine paleotemperatures.[9] Moreover, metastable fluids play important roles in industrial applications such as choked two-phase flows,[10] boiling liquid expanding vapor explosions,[11] and rapid phase transitions.[12] Despite their theoretical and practical importance, their ephemeral nature makes it difficult to evaluate properties in deeply metastable states.

For model systems, thermodynamic perturbation theories[13–15] can be developed which can accurately calculate both stable and metastable properties. For simple interaction potentials, several accurate equations of state exist, such as SAFT-VR Mie and its modifications,[16–19] and uv-theory.[20–22] For model systems with well-defined inter-action potentials, metastable properties can also be investigated in detail using molecular simulations. Restricted ensembles can be used to delay or prevent the spontaneous phase transformation, maintaining the metastable state sufficiently long to sample their properties.[23–27] In these ensembles, one stabilizes the fluid by prohibiting configurations that lead to spontaneous phase transition, and the thermodynamic properties are then available by averaging over the permissible states. One drawback is that the properties depend on the choice of restricted ensemble, albeit this dependence is in many cases small. An alternative, more direct method is to simulate the system in one of the standard ensembles and to stop sampling just before it phase-separates.[28–30] This strategy only works at moderate metastabilities.

Very often, the properties of a fluid in the metastable region are just estimated directly from an equation of state (EoS) regressed to data measured experimentally or simulated in the stable region. The extension of the equation of state into the metastable region is not free from spurious behaviors, such as the artificial, second Maxwell loop shown by multiparameter EoS.[31]

Despite the progress achieved in the theoretical and simulation characterization of metastable states for certain model systems,[32] simple and more general methods, applicable to arbitrary interaction potentials, real fluids and mixtures, are desirable.

Several works have noted that isochores, when plotted in temperature-pressure space, are quite linear.[33,34] Baidakov and Skripov[34] observed that this linearity continues to hold when crossing the liquid binodal into the

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superheated liquid region. It is in this context we place our contribution, by analyzing simple methods to evaluate the properties of metastable phases based on isochoric temperature expansion. The only ingredients involved are the thermal pressure coefficient and its temperature derivative, which can be straightforwardly evaluated either from the EoS, simulations or even experimental data in the stable region. In addition, we present a simple procedure to evaluate these coefficients directly by using molecular simulations in the canonical ensemble. Using this method, it is possible to map the properties of the whole metastable region just from one isotherm simulated at a reference temperature.

By comparing to simulation results for pure fluids and mixtures of Lennard-Jones fluids, we find that isochoric extrapolation methods are robust, reliable, and accurate. For real fluids, we verify a similar performance of the extrapolation behavior in the stable regime. In particular, we show that when this extrapolation is applied to the reference EoS of real water, IAPSW95,[35] it eliminates the controversial re-entrance of the liquid-vapor spinodal, predicting a monotonous decrease upon cooling. In another work,[36] we show that the extrapolation protocols presented in this work enable accurate estimation of surface properties when combined with multiparameter EoS and density gradient theory.

This work is organized as follows. In Sec. II we present the theoretical rationale of the isochoric extrapolation approach and specify the extrapolations that have been evaluated. In Sec. III, we introduce the method to evaluate the coefficients of the expansion directly from simulations and discuss the technical details of the molecular simulations. In Sec. IV we evaluate the accuracy of the extrapolation methods by comparing to simulation results, and also apply them to water as an example of a real fluid. Sec. V offers conclusions and outlook.

II. THEORY

To simplify notation we treat the case of a pure fluid, although the arguments also apply to a mixture with fixed composition. Consider a pure fluid of N particles in a volume V at temperature T. Thermodynamic properties such as the residual Helmholtz energy A^{res} and residual pressure $P^{\mathrm{res}} = -(\partial A^{\mathrm{res}}/\partial V)_T$ are rigorously given as sums (or integrals) over microstates:[13]

$$\beta A^{\mathrm{res}} = -\ln \sum_i \exp(-\beta U_i) \tag{1}$$

$$\beta P^{\mathrm{res}} = -\beta \frac{\sum_i (\partial U_i/\partial V) \exp(-\beta U_i)}{\sum_i \exp(-\beta U_i)} \tag{2}$$

where $\beta = 1/k_B T$, k_B is Boltzmann's constant and $U_i = U_i(V, N)$ is the potential energy of microstate i. The residual Helmholtz energy A^{res} and pressure P^{res} are just defined as the total Helmholtz energy A and pressure P minus the ideal gas contribution, e.g. $P^{\mathrm{res}} = P - \rho k_B T$

where ρ is the density. In statistical-mechanical expressions such as these, temperature T plays a different role than the extensive variables (V, N). Whereas changes in temperature determine the relative weights of microstates, changes in extensive variables (V, N) change the set of microstates altogether. Isochoric extrapolation strategies may therefore behave differently than isothermal expansion techniques such as the virial expansion. This motivates a comparison of the two approaches.

A. Isochoric extrapolation

We will evaluate two simple options for isochoric extrapolation. The first is a direct Taylor expansion of the pressure P in temperature up to second order:

$$\begin{aligned} P_{\mathrm{rec}}(T, v) = {} & P_{\mathrm{stb}}(T_{\mathrm{stb}}, v) + P_{\mathrm{stb}, T}(T_{\mathrm{stb}}, v)(T - T_{\mathrm{stb}}) \\ & + \frac{1}{2} P_{\mathrm{stb}, TT}(T_{\mathrm{stb}}, v)(T - T_{\mathrm{stb}})^2 \end{aligned} \tag{3}$$

where subscript rec denotes the *reconstructed* pressure in the metastable region, subscript stb refers to the stable starting state, and P_T and P_{TT} are the first and second-order derivatives of pressure with respect to temperature, holding molar volume v and composition constant. We refer to Eq. (3) as a T_2 **expansion**, and more generally an n-th order Taylor expansion as a T_n expansion.

The second extrapolation method is inspired by statistical-mechanical expressions such as Eq. (2) and the virial expansion (Eq. (16) below), which suggest Taylor-expanding βP in β, since the natural variables appearing in statistical mechanics are βP and β instead of P or T:

$$\begin{aligned} \beta P_{\mathrm{rec}}(T, v) = {} & (\beta P)_{\mathrm{stb}} + (\beta P)_{\mathrm{stb}, \beta}(\beta - \beta_{\mathrm{stb}}) \\ & + \frac{1}{2}(\beta P)_{\mathrm{stb}, \beta\beta}(\beta - \beta_{\mathrm{stb}})^2. \end{aligned} \tag{4}$$

We denote Eq. (4) a β_2 **expansion**, and β_n as the corresponding n-th order expansion. In terms of temperature, the β_2 expansion can also be written

$$\begin{aligned} P_{\mathrm{rec}}(T, v) = {} & P_{\mathrm{stb}}(T_{\mathrm{stb}}, v) + P_{\mathrm{stb}, T}(T_{\mathrm{stb}}, v)(T - T_{\mathrm{stb}}) \\ & + \frac{T_{\mathrm{stb}}}{2T} P_{\mathrm{stb}, TT}(T_{\mathrm{stb}}, v)(T - T_{\mathrm{stb}})^2. \end{aligned} \tag{5}$$

Evidently, the T_2 and β_2 expansions only differ by the scaling factor T_{stb}/T in the highest-order term. The zeroth-order expansions also differ, since the T_0 expansion is $P_{\mathrm{rec}} = P_{\mathrm{stb}}$ while the β_0 expansion is $P_{\mathrm{rec}} = P_{\mathrm{stb}}T/T_{\mathrm{stb}}$. The T_1 and β_1 expansions are, however, identical.

While the T_2 and β_2 expansions only go to second order in temperature, there is no conceptual limitation preventing the use of higher-order terms. The third-order Taylor expansions would require evaluating P_{TTT}, a fourth-order derivative of the Helmholtz energy. This quantity corresponds to a higher-order derivative of the Helmholtz energy than most directly measurable thermodynamic quantities, and is presumably associated with higher uncertainty.

We will next discuss some systems for which these extrapolation methods are exact. First, they are clearly exact for ideal gases. For an ideal gas, the β expansion is in fact exact already at zeroth order.

A more realistic description of a fluid is provided by the van der Waals equation of state

$$P = \frac{RT}{v - b} - \frac{a}{v^2}, \qquad (6)$$

where a and b depend only on composition, but not on density or temperature. In this case, the T_1 expansion becomes

$$P_{\text{rec}}(T, v) = P(T_{\text{stb}}, v) + P_T(T_{\text{stb}}, v)(T - T_{\text{stb}}) \qquad (7)$$

$$= \frac{RT_{\text{stb}}}{v - b} - \frac{a}{v^2} + \left(\frac{R}{v - b} \right)(T - T_{\text{stb}}) \qquad (8)$$

$$= \frac{RT}{v - b} - \frac{a}{v^2} \qquad (9)$$

and hence the T_1 expansion is exact for the van der Waals equation of state, and the same is true for the β_1 expansion. On the other hand, a Taylor expansion in density would require an infinite number of terms to be exact.

More generally, isochoric extrapolation is exact for systems where the potential energy is equal for all microstates, e.g. hard bodies immersed in a uniform background potential. Indeed, it follows from Eq. (1) that $-\beta A^{\text{res}}(T, V, N) = \ln \omega(V, N) - \beta U(V, N)$ where ω (the number of microstates) and U do not depend on temperature, and thus $\beta P = \omega_V / \omega - \beta U_V$. The T expansion and the β expansion will thus both be exact at first order. We therefore see that the argument for the van der Waals EoS does not hinge on its crude representation of the hard-sphere repulsion.

B. The starting point for isochoric extrapolation

We now discuss the starting point temperature for the extrapolation, T_{stb} (cf. Fig. 1). One is often interested in a range of metastable states at different densities, and the starting points can be described by a function $T_{\text{stb}}(v)$. A natural option is to perform an isochoric extrapolation from the binodal, i.e. choosing $T_{\text{stb}}(v) = T_{\text{sat}}(v)$, where subscript sat refers to saturation. The advantage of this choice is that it minimizes the temperature range that must be extrapolated across. What complicates starting from the binodal is that the saturation temperature is different for each density, and requires actually knowing the location of the binodal. There are certainly many mixtures for which the binodal is unknown.

A simpler choice is performing the extrapolation from a supercritical isotherm $T_{\text{stb}} = T_0$; i.e. starting the extrapolation from the same temperature T_0 for all densities. The choice of isotherm T_0 is in principle arbitrary, but should not be so high as to render attractive forces insignificant. A simple choice that seems to work well when
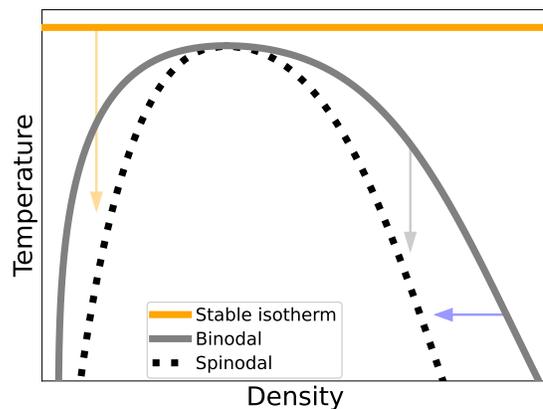
FIG. 1. Different ways of extrapolating into the metastable region. The gray curve is the binodal and the dotted curve the spinodal. The metastable region is enclosed by the binodal and the spinodal. The vertical arrows correspond to isochoric extrapolation, where the orange arrow starts from a supercritical isotherm, and the gray arrow starts from the binodal. The blue, horizontal arrow illustrates isothermal extrapolation from the binodal.

estimating metastable states is the critical temperature, i.e. $T_0 = T_c$, with the precaution of avoiding near-critical densities since P_{TT} may not be well-behaved, as discussed in the next section. We will see that, for the potentials examined, several choices of starting points in fact yield accurate estimation of metastable properties.

C. Evaluating the isochoric expansion coefficients

There are different routes to evaluate the coefficients appearing in the proposed isochoric expansion.

First, let's consider the case where an analytical expression of the EoS is known, either obtained from theoretical considerations or regressed from simulation or experimental data in the stable region. In this case, one can simply evaluate analytically or numerically the first and second order derivative of the pressure P at the reference temperature for the extrapolation T_{stb}. If an accurate EoS exists, this is by far the simplest option.

Other options rely on molecular simulation. First, note that the expansion coefficients are connected to other measurable thermodynamic quantities by Maxwell relations. Relevant Maxwell relations are

$$\left(\frac{\partial P^{\text{res}}}{\partial T} \right)_v = \left(\frac{\partial s^{\text{res}}}{\partial v} \right)_T \qquad (10)$$

$$\left(\frac{\partial (\beta P^{\text{res}})}{\partial \beta} \right)_v = - \left(\frac{\partial u^{\text{res}}}{\partial v} \right)_T \qquad (11)$$

$$\left(\frac{\partial^2 P^{\text{res}}}{\partial T^2} \right)_v = \frac{1}{T} \left(\frac{\partial c_v^{\text{res}}}{\partial v} \right)_T \qquad (12)$$

where s^{res}, u^{res}, c_v^{res} are the molar residual entropy, internal energy and isochoric heat capacity, respectively.

This means that if pressure, internal energy (or entropy) and isochoric heat capacity are correlated as functions of density along an isotherm, one can evaluate the coefficients needed to obtain an approximate equation of state $P = P(T, v)$ through e.g. the T_2 expansion. This could be especially convenient in the context of molecular simulations, since heat capacities and average internal energies are straightforward to sample in the canonical ensemble. In Sec. II C 1 we also show how to obtain these derivatives directly and more efficiently from simulations in the canonical ensemble.

Since P_{TT} is connected by Eq. (12) to the isochoric heat capacity which diverges at the critical point, this suggests that a second-order isochoric extrapolation may not be well-behaved if the stable starting state is chosen in the vicinity of the critical point. In fact, EoS generally fail to predict the divergence of c_v at the critical point, as this requires non-analytic terms.[37] Most EoS are fully analytical and therefore predict finite isochoric heat capacities at the critical point, with notable exceptions being the multiparameter EoS for water[35] and carbon dioxide.[38] Using an analytical EoS enables the use of a second-order isochoric expansion from the binodal, also in the critical region. Unlike P_{TT}, the first-order derivative P_T is continuous at the critical point, where it equals the limiting slope of the vapor pressure curve $P_{\text{sat}}(T)$.

1. Direct simulation method to evaluate the isochoric expansion coefficients

As noted in Sec. II C, one can evaluate the isochoric expansion coefficients by correlating pressure, internal energy and isochoric heat capacity along an isotherm, and then evaluate analytically or numerically the derivative with respect to the molar volume. Here we present another, more direct way to evaluate these coefficients directly from a canonical simulation. The coefficients can be calculated in a simulation performed at constant number of particles N, volume V and temperature T in terms of two quantities that are customarily monitored in those simulations: the potential energy U and the internal virial[39] divided by the volume V, i.e. $\mathcal{V} = \frac{1}{3V} \sum_{i=1}^{N} \boldsymbol{r}_i \cdot \boldsymbol{f}_i$, where $\boldsymbol{r}_i$ is the position of atom i and $\boldsymbol{f}_i$ is the net force on atom i due to all other atoms. More precisely the coefficients can be obtained by direct sampling:

$$P^{\text{res}} = \langle \mathcal{V} \rangle \tag{13}$$
$$P^{\text{res}}_{\beta} = -\operatorname{Cov}(U, \mathcal{V}) \tag{14}$$
$$P^{\text{res}}_{\beta\beta} = \operatorname{Cov}((U - \langle U \rangle)^2, \mathcal{V}) \tag{15}$$

where $\langle \ \rangle$ and $\operatorname{Cov}()$ are the ensemble average and covariance in the canonical ensemble. Whereas Eq. (13) and Eq. (14) are well-known,[39] we did not find a derivation of Eq. (15) in the literature. We therefore include a derivation in the supplementary material (SM), obtained by a third-order differentiation of the configurational partition function. The derivation can be straightforwardly

extended to evaluate any higher-order coefficients of the β or T-expansion, if needed.

Therefore, by simulating a single stable isotherm in the canonical ensemble, we can calculate directly the expansion coefficients needed to map the pressure in the whole region at lower temperature. If desirable, the residual Helmholtz energy can also be reconstructed as $a^{\text{res}}_{\text{rec}}(T, v) = -\int_0^v P^{\text{res}}_{\text{rec}}(T, v')dv'$. This requires much less effort than simulating several isotherms in the stable region, regressing all the data using a flexible functional form, and then extending it into the metastable region.

D. Isothermal extrapolation

To benchmark the performance of isochoric reconstruction, we compare with isothermal extrapolation methods. The latter is typically implemented as a Taylor expansion in either molar volume or density.

The virial expansion is an isothermal Taylor expansion from zero density:

$$\beta P = \rho + B_2(\beta)\rho^2 + B_3(\beta)\rho^3 + B_4(\beta)\rho^4 + \cdots . \tag{16}$$

The virial coefficients B_n can be rigorously calculated from the intermolecular potential via the partition functions of a finite number of particles.[13,40] For monatomic particles, the second virial coefficient is

$$B_2(\beta) = -2\pi \int_0^\infty (e^{-\beta u(r)} - 1)r^2 dr, \tag{17}$$

where u is the pair potential and r is the interparticle distance. For the van der Waals EoS one obtains $B_2^{\text{vdW}} = b - a\beta$. For a square-well potential one obtains $B_2^{\text{SW}} = c_0 \exp(\beta\epsilon) + c_1$ where c_0, c_1 are temperature-independent. These examples suggest including powers of β in isochoric extrapolation at low densities, which seems to favor a β expansion over a T expansion.

For liquids, at least a second-order polynomial in ρ or v is needed to predict a spinodal limit. Speedy[41] used such an approach to estimate the liquid spinodal of water. To predict metastable liquid properties, we have therefore also considered a second-order density expansion:

$$P_{\text{rec}}(T, \rho) = P_{\text{stb}}(T, \rho_{\text{stb}}) + P_{\text{stb},\rho}(T, \rho_{\text{stb}})(\rho - \rho_{\text{stb}}) + \frac{1}{2}P_{\text{stb},\rho\rho}(T, \rho_{\text{stb}})(\rho - \rho_{\text{stb}})^2 \tag{18}$$

which is most conveniently performed from the binodal, where $\rho_{\text{stb}} = \rho_{\text{sat}}$. We will denote this a $\boldsymbol{\rho_2}$ **expansion**, and it will be used to benchmark the performance of the isochoric extrapolation methods for both vapors and liquids.

III. SIMULATIONS

In order to test the validity and accuracy of the isochoric extrapolation and of the method proposed in Sec. II C 1 to

get the expansion coefficients, we have performed NVT Monte Carlo simulations for Lennard-Jones potentials. Starting from a face-centered cubic lattice, the system was equilibrated by running 10 simulation blocks, each block consisting of $5000 \times N_{\text{tot}}$ attempts to displace a random particle. The maximum displacement length of each component was independently adjusted to achieve an acceptance ratio between 30% and 50%. The production run consisted of 20 blocks, each consisting of $10^5 \times N_{\text{tot}}$ attempts to displace a random particle. For the reference isotherm at $T = 1.5$, the production run consisted of 150 blocks to ensure good statistics for $P_{\beta\beta}^{\text{res}}$, which exhibits relatively large fluctuations. All properties of interest were sampled after each 5th displacement attempt. Different versions of the Lennard-Jones potential were simulated, as explained in Sec. IV and the SM.

To illustrate the approach for mixtures, where equations of state are generally less accurate, we simulated two binary mixtures. These are denoted the S mixture and the E mixture, and are defined by

$$\sigma_{22} = \sigma_{11}/2, \qquad \varepsilon_{22} = \varepsilon_{11} \qquad \textbf{(S mixture)}$$

and

$$\sigma_{22} = \sigma_{11}, \qquad \varepsilon_{22} = \varepsilon_{11}/2 \qquad \textbf{(E mixture)}$$

where ϵ and σ denote the well-depth and particle size used in the LJ potentials. In both cases, $\varepsilon_{12} = \sqrt{\varepsilon_{11}\varepsilon_{22}}$ and $\sigma_{12} = (\sigma_{11}+\sigma_{22})/2$. Whereas the density and temperature will be varied, the composition will be fixed to: $z_1 = z_2 = 0.5$.

For mixtures, simulations were performed with a total number of particles of $N_{\text{tot}} = 500$, 250 of each component. Potential interactions were included up to a cutoff of $r_c = 3.5\sigma_{11}$ for all particles, and standard long-range corrections were applied.[39] Note that long-range corrections yield temperature-independent contributions to the pressure and the energy. We have used σ_{11} and ε_{11} to adimensionalize the simulation results in the usual way.

IV. RESULTS AND DISCUSSION

We now present and discuss the main results. A more comprehensive comparison of the extrapolation strategies is provided in the SM, including a table with results from all evaluated expansions. In the SM we also show results for the LJ-spline[21,42] potential, with similar conclusions as discussed here.

A. Lennard Jones-type fluids

To test the extrapolation methods described in Sec. II, we will compare them with simulation results for model fluids interacting via the LJ potential. To test the approach for pure fluids we consider the LJ potential truncated and shifted at 2.5σ (LJTS2.5σ), which is a frequently used

benchmark fluid in the literature.[43] In the calculations with LJTS2.5σ, we have used the empirical, multiparameter EoS by Thol et al.,[44] while the simulations are from Ref.[43] The expansion coefficients were calculated directly by taking the derivatives of the equation of state by Thol et al.[44] In the following, densities and temperatures are given in Lennard Jones units.

Figure 2 compares the simulation results in the metastable region from Ref.,[43] the equation of state by Thol et al.,[44] and the T_2 and β_2 isochoric extrapolations starting from $T_{\text{stb}} = 1.5$, approximately equal to $1.38T_c$. This high starting temperature is chosen merely to distinguish the different extrapolations, and does not yield optimal accuracy. Notice that the equation of state predicts the existence of a second loop in the metastable and unstable region, which is not present in the isochoric extrapolations.

To quantify the accuracy of the extrapolation schemes we use the mean normalized error

$$\bar{Z} = \frac{1}{N_{\text{sim}}} \sum_{i=1}^{N_{\text{sim}}} \frac{|P_{\text{rec}}^{(i)} - P_{\text{sim}}^{(i)}|}{\sigma_{\text{sim}}^{(i)}} \tag{19}$$

where the sum is over the N_{sim} metastable simulations, $\sigma_{\text{sim}}^{(i)}$ is the stated uncertainty of simulation i by Heier et al.,[43] and the sum includes all four temperatures (0.7, 0.8, 0.9, 1.0). The results are shown in Fig. 3, in separate plots for the vapor and the liquid. Evidently most extrapolation schemes yield a high and comparable accuracy when extrapolating from the binodal. The exception is the ρ_2 expansion in the liquid phase, exhibiting 3-4 times higher error than the other expansions. The small differences between the other binodal expansions could be due to inaccuracies in the simulated pressures and their uncertainty estimates, or in the calculated derivatives from the EoS. When extrapolating from several different starting points, however, a clear picture emerges: the T_2 expansion is superior in the liquid phase, and the β_2 expansion is superior for describing the behavior in the vapor phase. In the SM we have replotted Fig. 3 using another equation of state (the PeTS EoS[43]) to calculate the coefficients of the expansion, with similar conclusions.

To see the effect of increasing the order of extrapolation, we have also evaluated the T_1 and T_3 expansions (Fig. 3). Given its simplicity, the high accuracy of the T_1 expansion when extrapolating from the binodal is especially striking. Although both the T_1 and T_3 expansions are excellent when extrapolating from the binodal, their performance is inferior to the T_2 expansion when starting from higher temperatures. For the T_1 expansion this is due to the inherent nonlinearity of the pressure isochore at high temperatures. For the T_3 expansion this may be due to the EoS' inaccurate representation of P_{TTT}, which is amplified by the $(T - T_{\text{stb}})^3$ factor as $|T - T_{\text{stb}}|$ increases.

We have also tested the virial expansion up to fourth order for the vapor phase, using the coefficients from Shaul et al.[45] The best results were obtained at third order, but at $\bar{Z} = 0.95$ this was still notably worse than

the other extrapolation schemes. When inspecting the lowest temperature $T = 0.7$ in detail, the second-order expansion is best, whereas the third and fourth-order expansions are progressively worse.

Next, we compare the T_2 and β_2 expansions with the ρ_2 expansions (Fig. 4). To have a consistent comparison, all expansions start from the binodal. Figure 4 shows that the ρ_2 expansion is clearly less accurate than the T_2 expansion at high metastabilities in the liquid phase. Both the T_2 and the β_2 expansions from the binodal yield metastable pressures that are almost identical with the EoS in the metastable regions where simulation data are available.

Figure 5 shows results for mixtures. Here, the extrapolation is performed from $T = 1.5$ at discrete densities. These results were obtained by use of Monte Carlo simulation with direct sampling of the expansion coefficients using Eqs. (13)–(15). Since the extrapolations (stars and hexagons) lie close to the simulations (circles), we confirm that the isochoric extrapolations offer similar performance for mixtures as for single-component fluids. Also for the mixtures, we observe a clear superiority of the β_2 expansion at low densities, whereas the T_2 expansion is slightly better at high densities. In the SM, this is quantified with mean normalized errors.

For the S mixture, the good agreement between the extrapolation and simulation results at $T = 1.25$ is striking. For $\rho > 0.4$ the system is mechanically unstable since $(\partial P/\partial \rho)_T < 0$, but the isochoric extrapolation still manages to achieve a reasonable prediction of the average properties.

Interestingly, the pressures of systems in the thermodynamically unstable region that remain single-phase due to finite-size effects[46,47] are also predicted well by the extrapolations. An example is the $T = 1.25$ isotherm for the S mixture (see SM for more details). We interpret this as finite-size effects of the system that suppress phase separation, with the resultant homogenized phase being similar to its isochoric neighbor at the higher temperature $T = 1.5$. This suggests that we can interpret isochoric extrapolation as yielding the properties of a homogenized phase. In the SM we also demonstrate that isochoric extrapolation agrees well with the constrained ensemble simulations by Corti and Debenedetti,[24] which partitions the simulation volume into small boxes, constraining the allowed density fluctuations in each box.

B. Real fluids - water

Real fluids differ from the LJ fluid in many aspects, such as many-body effects, quantum effects, and generally incomplete knowledge of the underlying interactions between the particles. Still, the properties of fluids can be accurately measured and correlated in the thermodynamically stable region, which makes isochoric extrapolation possible. Although there are experimental fluid data available in the metastable regions,[48] they are mostly at low

metastabilities,[49] since the time scale of homogeneous nucleation becomes too short for experimental observation at high metastabilities.

One of the fluids whose properties have been characterized with greater accuracy is water. Water is also remarkable due to the anomalous behavior of many of its properties.[50] Accurate description of the thermodynamic properties of water with molecular perturbation theory remains an unsolved challenge.[51,52] This is attributed to difficulties in capturing structural changes upon activation of hydrogen bonds at low temperatures. This is inconsistent with perturbation theory's implicit assumption that the structure is primarily controlled by repulsive interactions.[52]

Different scenarios have been proposed to explain the thermodynamic anomalies of water.[4,53] Some of these scenarios are associated with a re-entrant behavior of the liquid-vapor spinodal,[41,54–56] consistent with the most popular empirical equations of state for water compiled by the International Association for the Properties of Water and Steam (IAPWS).[35] We have used a T_2 expansion of the IAPWS95 equation of state[35] to evaluate the liquid-vapor spinodal for real water. To ensure high accuracy, the coefficients were evaluated using the binodal as starting point; extrapolating from a supercritical isotherm yields qualitatively similar results.

Figure 6 shows that a second-order temperature expansion of the IAPWS95 equation of state[35] yields a monotonically decreasing liquid-vapor spinodal for water, contrary to the re-entrant behavior predicted by the direct application of the IAPWS95 equation of state in the metastable region. This is the same behavior obtained from common intermolecular potential models developed for water,[56] including TIP4P/2005 which is the one reproducing most closely the properties of real water.[57] This is also the behavior expected by the liquid-liquid critical point and singularity-free scenarios.[4,53]

V. CONCLUSIONS

Thermodynamic properties of fluids in the metastable region of the phase diagram are needed in a wide range of applications. In particular, they are crucial to have accurate predictions of nucleation rates. But they are typically very difficult to evaluate precisely because the propensity of metastable states to transform quickly and spontaneously into the most stable phase. This work has evaluated methods for estimating metastable properties by extrapolation from stable states. We presented two isochoric extrapolation protocols: the T_n expansion which Taylor-expands P in T, and the β_n expansion that Taylor-expands βP in $\beta = 1/k_B T$, where subscript n refers to the order of the Taylor expansion. Notably, they become exact for important model systems such as the van der Waals equation of state, and accurately reproduce metastable pressures from molecular simulations.

We investigated different starting points of the extrap-
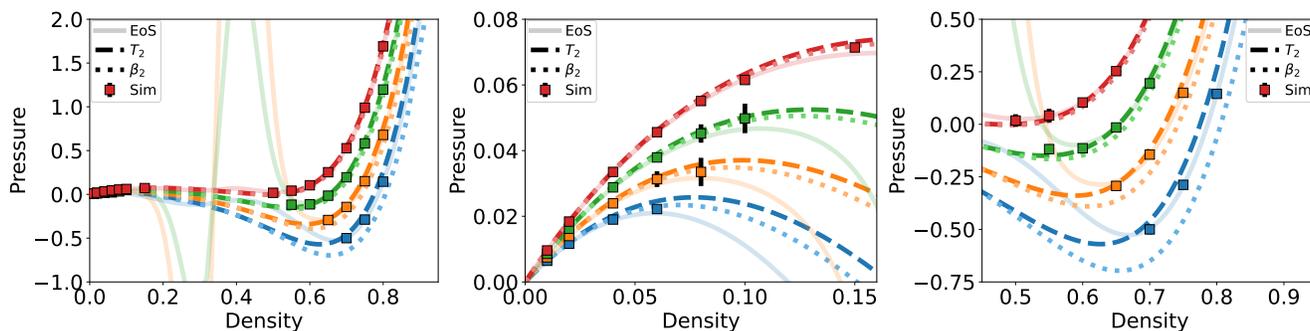
FIG. 2. Comparison of LJTS2.5σ simulation results from Ref.[43] (symbols), the EoS by Thol et al.[44] (solid lines) and the T_2 and β_2 extrapolations (dashed and dotted lines) from the temperature $T = 1.5$, which is 38% above the critical temperature. Colors correspond to temperatures 0.7 (blue), 0.8 (orange), 0.9 (green) and 1.0 (red). The left panel shows all densities, the middle and right panels zoom in on vapor and liquid densities, respectively.
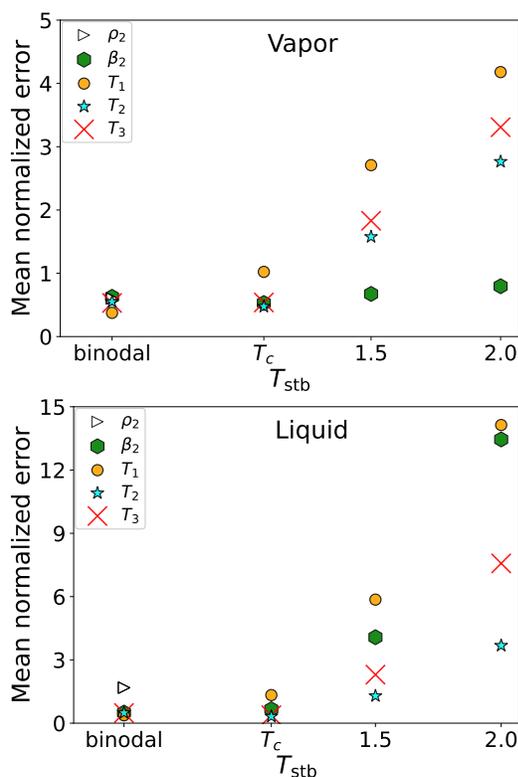
FIG. 3. Mean normalized error $\bar{Z}$ for several extrapolation schemes, plotted against the starting point of the extrapolation. Extrapolations were calculated using the Thol et al. EoS,[44] while the metastable simulations and their uncertainties were taken from Heier et al.[43]

olations, different equation of state, and different variants of the Lennard-Jones system, including both pure fluids and mixtures. For metastable liquids, the T_2 expansion was most accurate, whereas for supersaturated vapors the β_2 expansion was most accurate. Starting from the closest temperature possible, typically at the binodal, generally yielded the highest accuracy, and in this case even the T_1 extrapolation was highly accurate.

We have also presented a method to evaluate all the isochoric expansion coefficients directly from a simple canonical ensemble NVT Monte Carlo or Molecular Dynamics simulation. This method can be used to map the properties of the whole metastable and unstable region from a single isotherm, which is appealing for complex intermolecular potentials where simulations are demanding.

Molecular-thermodynamic perturbation theories exist that are able to calculate metastable properties, such as uv-theory and SAFT-VR Mie. Through extrapolation, any equation of state can be used to predict metastable properties, also those with sole focus on accuracy for stable states.

Isochoric extrapolation was also used to predict the mechanical stability limit, i.e. the thermodynamic spinodal. For real water, the liquid spinodal was predicted to be monotonic, in contrast to the re-entrant behavior suggested by the direct extension of the multiparameter EoS. The existence of a re-entrant spinodal is the cornerstone supporting different scenarios to justify water anomalies. The use of this extrapolation to evaluate other properties of water in the deeply metastable region could shed light on the different scenarios proposed to explain water anomalies.

Since isochoric extrapolation yields an isotherm that is well-behaved also in the unstable region, it can be used in density gradient theory to improve the evaluation of important properties such as the surface tension; this approach is explored in detail in another work.[36]

The present work is a step toward rational guidelines for estimating metastable fluid properties. Future work should investigate whether there are better functional forms for isochoric extrapolation of pressure, or whether it is more fruitful to extrapolate other properties such as c_v. Another option is to explore multivariate expansions in density and temperature. To more rigorously test the extrapolation methods, it will be beneficial to consider more complex interaction potentials, such as those involving hydrogen bonding, three body interactions, and quantum effects.
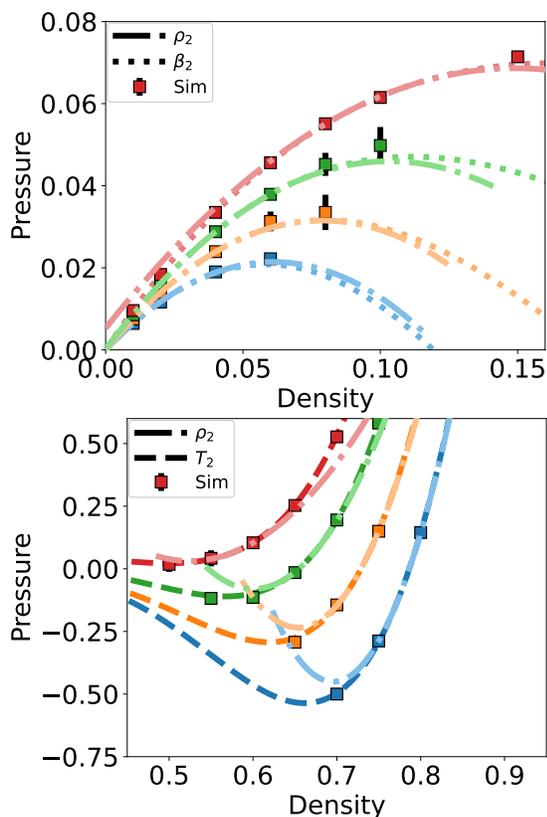
FIG. 4. Comparison of isochoric extrapolation (dashed lines) and second-order density expansion (dash-dot lines) from the binodal of the LJTS2.5σ fluid. The isochoric expansions coincide with simulations (symbols) within their error bars, whereas the ρ_2 expansion deviates from simulations at the highest metastabilities. Since the T_2 and β_2 expansions would be indistinguishable in the plots, we only show one of them in each panel. Colors correspond to temperatures 0.7 (blue), 0.8 (orange), 0.9 (green) and 1.0 (red).

FIG. 5. Extrapolation of pressure for the E mixture (top) and the S mixture (bottom), where each color is associated with a different temperature. Circles are simulation results, while stars and hexagons are respectively T_2 and β_2 extrapolations from $T = 1.5$ (black).

SUPPLEMENTARY MATERIAL

The supplementary material contains the derivation of the sampling formulas for the isochoric expansion coefficients, the new simulation results, and more detailed results for the Lennard Jones fluids.

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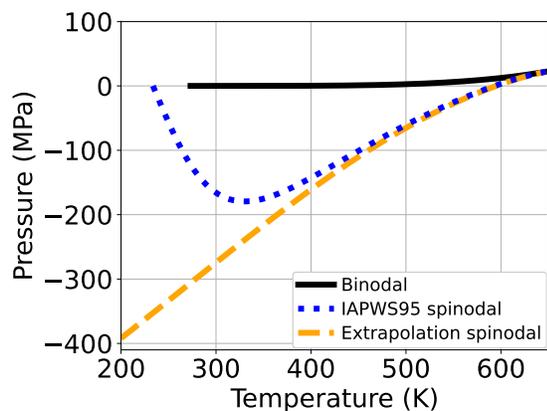
FIG. 6. Binodal (solid line) and liquid spinodal of water calculated from the IAPWS95 EoS[35] (dotted line). The spinodal represented by the dashed line is obtained by T_2 extrapolation from the binodal.

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