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Rigorous expressions for thermodynamic properties in the *NpH* ensemble

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Molecular expressions for thermodynamic properties of fluids and derivatives of the entropy up to third order in the isoenthalpic-isobaric ensemble are derived by using the methodology developed by Lustig for the microcanonical and canonical ensembles [J. Chem. Phys. **100**, 3048 (1994); Mol. Phys. **110**, 3041 (2012)]. They are expressed in a systematic way by phase-space functions, which represent derivatives of the phase-space volume with respect to enthalpy and pressure. The expressions for thermodynamic properties contain only ensemble averages of combinations of the kinetic energy and volume of the system. Thus, the calculation of thermodynamic properties in the isoenthalpic-isobaric ensemble does not require volume derivatives of the potential energy. This is particularly advantageous in Monte Carlo simulations when the interactions between molecules are described by very accurate *ab initio* pair and nonadditive three-body potentials. The derived expressions are validated by Monte Carlo simulations for the simple Lennard-Jones model fluid as a test case.

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I. INTRODUCTION

The isoenthalpic-isobaric (NpH) ensemble, in which the entropy is the thermodynamic potential and the number of particles, N, the pressure p, and the enthalpy H are the independent variables, was first proposed by Byers Brown in 1958 [1]. As the microcanonical (NVE) ensemble, it is a so-called shell ensemble, because the system is bound to a hypersurface of constant enthalpy in phase space. Within the Laplace-Legendre transformation scheme of the eight basic ensembles of statistical mechanics described by Graben and Ray [2], it is related to the isothermal-isobaric (NpT) ensemble in the same way as the microcanonical ensemble is related to the canonical (NVT) ensemble. The NpH ensemble has received less attention than the more familiar microcanonical, canonical, grand canonical, or NpT ensembles, but, as it is the elementary ensemble among the constant pressure ensembles, it should be given proper consideration. It is the aim of this work to provide rigorous molecular expressions for the calculation of common thermodynamic properties of fluids by Monte Carlo simulations in the NpH ensemble.

In 1980, Andersen developed an algorithm for molecular-dynamics simulations of fluids in the NpH ensemble [3]. Motivated by Andersen's work, Haile and Graben [4] applied the fluctuation theory for transforming ensemble averages between different ensembles devised by Lebowitz *et al.* [5] to derive expressions for the isobaric heat capacity and isentropic compressibility in terms of fluctuations in the kinetic energy and volume in the NpH ensemble from known expressions for the NpT and microcanonical ensembles. Subsequently, Ray *et al.* [6] formulated the fundamental statistical-mechanical relations for the NpH ensemble and devised a method for the direct derivation of expressions for thermodynamic properties from the probability density of the NpH ensemble. They obtained the same expressions as Haile and Graben [4] for the isobaric heat capacity and isentropic compressibility, and additionally provided an expression for the isobaric expansion coefficient. After Pearson *et al.* [7] had developed a Laplace transform technique in 1985 to evaluate the integrals over the momenta in the partition function of the microcanonical ensemble, Ray and Graben [8] applied this method to the NpH ensemble and derived rigorous expressions for the isobaric heat capacity, isentropic compressibility, and isobaric expansion coefficient. They showed that, in the thermodynamic limit $N \to \infty$, these expressions asymptotically converge to those previously derived by Haile and Graben [4] and Ray *et al.* [6].

The NpH ensemble has for instance been applied in molecular simulations to calculate properties of the hard sphere gas [9,10] or the Joule-Thomson inversion curve of hydrogen sulfide [11]. The Joule-Thomson inversion curve is a characteristic curve in a pressure-temperature diagram of a fluid, along which the Joule-Thomson coefficient is zero. Since the Joule-Thomson coefficient is the derivative of temperature with respect to pressure at constant enthalpy, that is, it is a function of the independent variables pressure and enthalpy, it can readily be calculated in the NpH ensemble. Implementations of the Gibbs ensemble Monte Carlo method in the NpH ensemble to study vapor-liquid equilibria of pure fluids [12] and mixtures [13] have also been proposed. Escobedo [14] developed a general framework with which advanced Monte Carlo methods such as multihistogram reweighting and replica-exchange methods can be applied to different shell ensembles including the NpH ensemble. Solca *et al.* [15] determined the melting pressure curve of argon by nonequilibrium molecular-dynamics simulations in the NpH

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ensemble. Molecular-dynamics or Monte Carlo algorithms for simulations in the *NpH* ensemble are implemented in the open-source molecular simulation tools LAMMPS [16], GROMACS [17], and MS2 [18].

The *NpH* ensemble also served as origin for the development of ensembles for the simulation of properties of crystalline solids. Parrinello and Rahman [19] extended the molecular-dynamics algorithm of Andersen to anisotropic solid media under uniform hydrostatic pressure by allowing not only for changes in size, but also in shape of the simulation cell. They also generalized the *NpH* ensemble to the *NσH* ensemble [20], in which the components of the stress tensor $\boldsymbol{\sigma}$ instead of the pressure are independent variables, and provided equations for the calculation of the adiabatic elastic compliances in terms of fluctuations of the elastic strains [21]. Subsequently, Ray [22] derived fluctuation formulas for the heat capacity and thermal expansion tensor at constant stress as well as the third-order elastic compliance tensor. Ray [23] also suggested a modification of the Hamiltonian proposed by Parrinello and Rahman [20] for the *NσH* ensemble so that it agrees with Anderson's Hamiltonian for the *NpH* ensemble in the case of an isotropic solid under uniform hydrostatic pressure. Ray and Rahman [24] modified the theory of the *NσH* ensemble to bring it into agreement with the theory of finite elasticity. They replaced the stress tensor by the tensor of thermodynamic tension **t** and introduced the undeformed state as reference state, which led to the $N\mathbf{t}H$ ensemble. The development of ensembles for the simulation of solid media from the *NpH* ensemble was summarized by Ray [25].

Based on the works of Pearson *et al.* [7] and Cağin and Ray [26], Lustig [27–31] developed a rigorous methodology to derive expressions for thermodynamic properties in the molecular-dynamics and microcanonical ensembles. By introducing so-called phase-space functions, which represent derivatives of the partition functions with respect to the independent variables, Lustig obtained expressions for thermodynamic properties in terms of the kinetic energy, potential energy, and volume derivatives of the potential energy of the system in a systematic way. With this methodology, essentially exact expressions for all thermodynamic properties and derivatives of arbitrary order of the thermodynamic potential in an ensemble can be derived. Recently, it has also been applied to derive rigorous expressions for thermodynamic properties in the canonical ensemble by Lustig [32,33], in the isothermal-isobaric (NpT) ensemble by Ströker *et al.* [34], and in the grand canonical (μVT) ensemble by Ströker and Meier [35]. The formalism for the microcanonical molecular-dynamics ensemble was for example applied by Mausbach and May [36] and the one for the canonical ensemble by Thol *et al.* [37], Vlasiuk *et al.* [38], and Deiters and Sadus [39]. In this article, we continue our previous work and apply the Lustig methodology to derive rigorous expressions for thermodynamic properties and derivatives of the entropy up to third order in the *NpH* ensemble.

The outline of this article is as follows. Section II provides the theoretical background for the calculation of thermodynamic properties in the *NpH* ensemble and presents expressions for thermodynamic properties in terms of phase-space functions, explicit expressions for the most important phase-space functions in terms of ensemble averages of combinations of kinetic energy and volume, and a general expression for phase-space functions of arbitrary order. The derived equations are validated by Monte Carlo simulations at three state points of the Lennard-Jones model fluid in Sec. III. Conclusions are presented in Sec. IV.

II. EXPRESSIONS FOR THERMODYNAMIC PROPERTIES

In analogy to the microcanonical ensemble, the phase-space volume for a system of spherical particles in the *NpH* ensemble is defined by

$$\Omega = \frac{1}{N!h^{3N}} \int_0^\infty \iint \frac{N}{V}\, \Theta(H - \mathscr{H} - pV) d\mathbf{r}^N d\mathbf{p}^N dV, \quad (1)$$

where h is the Planck constant, V is the volume, $\mathscr{H} = K + U$ is the Hamiltonian of the corresponding microcanonical system with kinetic energy K and potential energy U, N/V is the volume scale, and $d\mathbf{r}^N$ and $d\mathbf{p}^N$ represent integrations over the $3N$ coordinates and momenta of the particles. The symbol $\Theta(x)$ denotes the Heaviside step function, which is unity for $x \geqslant 0$ or zero for $x < 0$. The phase-space density $\omega = \partial\Omega/\partial H$ is the partial derivative of the phase-space volume with respect to enthalpy. It is given by

$$\omega = \frac{1}{N!h^{3N}} \int_0^\infty \iint \frac{N}{V}\, \delta(H - \mathscr{H} - pV) d\mathbf{r}^N d\mathbf{p}^N dV, \quad (2)$$

in which $\delta(x)$ denotes the Dirac delta function. Since the volume is not constant but fluctuates in the *NpH* ensemble, the number of dimensions of the phase space of the *NpH* ensemble is larger by one compared to the microcanonical ensemble, in which the volume is constant. Hence, the phase-space volume and phase-space density include an integration over all volumes that are accessible to the system, i.e., from zero to infinity. This integration introduces the unit of volume into the phase-space volume and phase-space density, which must be compensated for by an appropriately chosen volume scale, so that both quantities are dimensionless. The volume scale for the closely related isothermal-isobaric ensemble was controversially discussed in the literature [40–43]. This controversy was finally resolved by Han and Son [42], who showed that N/V is the correct volume scale for homogeneous systems simulated in periodic boundary conditions. Therefore, we adopt N/V as the volume scale also for the *NpH* ensemble as in our previous work on the isothermal-isobaric ensemble [34].

Becker [44] and Münster [45] pointed out that the entropy in the microcanonical ensemble can either be defined by the phase-space volume or by the phase-space density. It has been controversially discussed in the literature which entropy definition is correct, e.g., in Refs. [28,46–50]. Some authors prefer the phase-space volume [7,26,47,48,51], whereas others use the phase-space density [28,45,49,50,52]. Lustig [30,31,46] examined the question of which entropy definition is best by molecular-dynamics and Monte Carlo simulations for the Lennard-Jones model fluid, but his studies did not yield a conclusive solution.

As the *NpH* ensemble is also an adiabatic ensemble, the entropy can analogously be defined in two ways, either with the phase-space volume by

$$S \overset{\Omega}{=} k_\mathrm{B} \ln \Omega(N, p, H), \tag{3}$$

or with the phase-space density by

$$S \overset{\omega}{=} k_\mathrm{B} \ln \omega(N, p, H), \tag{4}$$

where k_B denotes the Boltzmann constant. Becker [44] argued that, in the microcanonical ensemble, both entropy definitions become equivalent in the thermodynamic limit because

$$\lim_{N\to\infty} \frac{\ln \Omega}{N} = \lim_{N\to\infty} \frac{\ln \omega}{N}, \tag{5}$$

that is, in the thermodynamic limit the phase-space volume becomes equivalent to a very thin shell near the hypersurface of constant energy. This argument also applies to the *NpH* ensemble, in which the phase-space volume becomes equivalent to a very thin shell near the hypersurface of constant enthalpy in the thermodynamic limit. Since we are interested in calculating properties of macroscopic systems, either entropy definition can be used as a starting point for the derivation of expressions for thermodynamic properties. Therefore, we develop the formalism for both entropy definitions. Both formalisms yield different equations for thermodynamic properties, which we distinguish in the remainder of this work by the notations $\overset{\Omega}{=}$ and $\overset{\omega}{=}$. Their numerical equivalence in the thermodynamic limit will be shown in Sec. III.

The derivation of expressions for thermodynamic properties in the remainder of this section proceeds in two steps. First, derivatives of the entropy with respect to the independent variables enthalpy and pressure and equations for thermodynamic properties are expressed by phase-space functions. Second, expressions for the phase-space functions in terms of ensemble averages of combinations of instantaneous values of the kinetic energy and volume of the system are obtained by comparing the corresponding derivatives of the phase-space volume to a general equation for an ensemble average in the *NpH* ensemble.

In the first step, derivatives of the entropy with respect to enthalpy and pressure are expressed in a systematic way by derivatives of the phase-space volume Ω or phase-space density ω by introducing the abbreviations

$$\mathcal{S}_{mn} \overset{\Omega}{=} \frac{\partial^{m+n} \ln \Omega}{\partial H^m \partial p^n}, \quad m, n = 0, 1, 2, \ldots, \tag{6}$$

$$\mathcal{S}_{mn} \overset{\omega}{=} \frac{\partial^{m+n} \ln \omega}{\partial H^m \partial p^n}, \quad m, n = 0, 1, 2, \ldots. \tag{7}$$

Moreover, derivatives of the phase-space volume are represented by the phase-space functions Ω_{mn} of the *NpH* ensemble, which are defined by

$$\Omega_{mn} = \frac{1}{\omega} \frac{\partial^{m+n}\Omega}{\partial H^m \partial p^n}, \quad m, n = 0, 1, 2, \ldots, \tag{8}$$

with the special cases $\Omega_{00} = \Omega/\omega$ and $\Omega_{10} = 1$. The inverse phase-space density is used in this definition because it also appears below in the general equation for an ensemble average in the *NpH* ensemble. Applying the product rule to Eq. (8) yields the two recursion relations

$$\frac{\partial \Omega_{mn}}{\partial H} = \Omega_{m+1,n} - \Omega_{20}\Omega_{mn}, \quad m + n \geqslant 1, \tag{9}$$

$$\frac{\partial \Omega_{mn}}{\partial p} = \Omega_{m,n+1} - \Omega_{11}\Omega_{mn}, \quad m + n \geqslant 1, \tag{10}$$

which are useful for calculating higher-order derivatives $\mathcal{S}_{mn}$. Using the definition of the entropy by the phase-space volume, Eq. (3), the first derivative of the entropy with respect to enthalpy is given by

$$\mathcal{S}_{10} \overset{\Omega}{=} \frac{\partial \ln \Omega}{\partial H} = \frac{1}{\Omega}\frac{\partial \Omega}{\partial H} = \frac{\omega}{\Omega}\frac{1}{\omega}\frac{\partial \Omega}{\partial H} = \frac{\omega}{\Omega} = \Omega_{00}^{-1}, \tag{11}$$

where the relation $\omega = \partial\Omega/\partial H$ has been applied. Accordingly, differentiating the entropy with respect to pressure yields

$$\mathcal{S}_{01} \overset{\Omega}{=} \frac{\partial \ln \Omega}{\partial p} = \frac{1}{\Omega}\frac{\partial \Omega}{\partial p} = \frac{\omega}{\Omega}\frac{1}{\omega}\frac{\partial \Omega}{\partial p} = \Omega_{00}^{-1}\Omega_{01}. \tag{12}$$

Applying the definition of the entropy in terms of the phase-space density, Eq. (4), the first derivatives are obtained as

$$\mathcal{S}_{10} \overset{\omega}{=} \frac{\partial \ln \omega}{\partial H} = \frac{1}{\omega}\frac{\partial \omega}{\partial H} = \frac{1}{\omega}\frac{\partial^2 \Omega}{\partial H^2} = \Omega_{20} \tag{13}$$

and

$$\mathcal{S}_{01} \overset{\omega}{=} \frac{\partial \ln \omega}{\partial p} = \frac{1}{\omega}\frac{\partial \omega}{\partial p} = \frac{1}{\omega}\frac{\partial^2 \Omega}{\partial p \partial H} = \Omega_{11}. \tag{14}$$

Using these results as starting points, the recursion relations, Eqs. (9) and (10), can be applied to successively obtain derivatives of higher order for both definitions of the entropy. Expressions for derivatives up to third order are presented in Table I. Some expressions simplify since $\Omega_{10} = 1$. The relations have the same mathematical structure as the corresponding relations for derivatives of the entropy in the microcanonical ensemble [33] with the volume and energy in the microcanonical ensemble being replaced by the pressure and enthalpy in the *NpH* ensemble.

The expressions for S_{mn} for both entropy definitions are interrelated to each other since the same definition for the phase-space functions is used in both formalisms. In order to transform expressions for S_{mn} for the definition with the phase-space volume Ω into those for the definition with the phase-space density ω, the correspondence

$$\Omega_{mn} \to \Omega_{m+1,n}\Omega_{20}^{-1} \tag{15}$$

must be applied to all phase-space functions in the expressions for the definition with Ω. This correspondence can be established by the following consideration. The entropy derivatives have the same mathematical structure when $\mathcal{S}_{mn}$ for the definition with Ω is expressed by derivatives of Ω and $\mathcal{S}_{mn}$ for the definition with ω by derivatives of ω. In the $\mathcal{S}_{mn}$ for the definition with the phase-space volume, each term $\Omega^{-1}(\partial^{m+n}\Omega/\partial H^m \partial p^n)$ must be extended by ω before phase-space functions can be introduced, which yields $(\omega/\Omega)\omega^{-1}(\partial^{m+n}\Omega/\partial H^m \partial p^n) = \Omega_{00}^{-1}\Omega_{mn}$. In the corresponding S_{mn} for the definition with the phase-space density, the derivative of the phase-space density in each term $\omega^{-1}(\partial^{m+n}\omega/\partial H^m \partial p^n)$ must be replaced by a derivative of Ω, which increases the order of the derivative with respect to enthalpy by one since $\omega = \partial\Omega/\partial H$. Hence, the terms become $\omega^{-1}(\partial^{m+1+n}\Omega/\partial H^{m+1}\partial p^n) = \Omega_{m+1,n}$. If all phase-space functions Ω_{10} were retained in the expression for $\mathcal{S}_{mn}$,

TABLE I. Expressions for derivatives $\mathcal{S}_{mn}$ up to third order in terms of phase-space functions Ω_{mn} for both entropy definitions.

$S \overset{\Omega}{=} k_\mathrm{B} \ln \Omega$	$S \overset{\omega}{=} k_\mathrm{B} \ln \omega$
$\mathcal{S}_{10} \overset{\Omega}{=} \Omega_{00}^{-1}$	$\mathcal{S}_{10} \overset{\omega}{=} \Omega_{20}$
$\mathcal{S}_{20} \overset{\Omega}{=} -\Omega_{00}^{-2} + \Omega_{00}^{-1}\Omega_{20}$	$\mathcal{S}_{20} \overset{\omega}{=} -\Omega_{20}^{2} + \Omega_{30}$
$\mathcal{S}_{30} \overset{\Omega}{=} 2\Omega_{00}^{-3} - 3\Omega_{00}^{-2}\Omega_{20} + \Omega_{00}^{-1}\Omega_{30}$	$\mathcal{S}_{30} \overset{\omega}{=} 2\Omega_{20}^{3} - 3\Omega_{20}\Omega_{30} + \Omega_{40}$
$\mathcal{S}_{01} \overset{\Omega}{=} \Omega_{00}^{-1}\Omega_{01}$	$\mathcal{S}_{01} \overset{\omega}{=} \Omega_{11}$
$\mathcal{S}_{02} \overset{\Omega}{=} -\Omega_{00}^{-2}\Omega_{01}^{2} + \Omega_{00}^{-1}\Omega_{02}$	$\mathcal{S}_{02} \overset{\omega}{=} \Omega_{12} - \Omega_{11}^{2}$
$\mathcal{S}_{03} \overset{\Omega}{=} 2\Omega_{00}^{-3}\Omega_{01}^{3} - 3\Omega_{00}^{-2}\Omega_{01}\Omega_{02} + \Omega_{00}^{-1}\Omega_{03}$	$\mathcal{S}_{03} \overset{\omega}{=} 2\Omega_{11}^{3} - 3\Omega_{12}\Omega_{11} + \Omega_{13}$
$\mathcal{S}_{11} \overset{\Omega}{=} -\Omega_{00}^{-2}\Omega_{01} + \Omega_{00}^{-1}\Omega_{11}$	$\mathcal{S}_{11} \overset{\omega}{=} -\Omega_{20}\Omega_{11} + \Omega_{21}$
$\mathcal{S}_{12} \overset{\Omega}{=} 2\Omega_{00}^{-3}\Omega_{01}^{2} - 2\Omega_{00}^{-2}\Omega_{11}\Omega_{01} - \Omega_{00}^{-2}\Omega_{02} + \Omega_{00}^{-1}\Omega_{12}$	$\mathcal{S}_{12} \overset{\omega}{=} 2\Omega_{20}\Omega_{11}^{2} - 2\Omega_{21}\Omega_{11} - \Omega_{20}\Omega_{12} + \Omega_{22}$
$\mathcal{S}_{21} \overset{\Omega}{=} 2\Omega_{00}^{-3}\Omega_{01} - \Omega_{00}^{-2}\Omega_{20}\Omega_{01} - 2\Omega_{00}^{-2}\Omega_{11} + \Omega_{00}^{-1}\Omega_{21}$	$\mathcal{S}_{21} \overset{\omega}{=} 2\Omega_{20}^{2}\Omega_{11} - \Omega_{30}\Omega_{11} - 2\Omega_{20}\Omega_{21} + \Omega_{31}$

the correspondence would simply read $\Omega_{mn} \to \Omega_{m+1,n}$ because Ω_{00} transforms into $\Omega_{10} = 1$. However, since Ω_{10} is replaced by unity, Ω_{20}^{-1} must be introduced into Eq. (15) to account for the correspondence $\Omega_{10} \to \Omega_{20}$. For the inverse transformation of an expression for $\mathcal{S}_{mn}$ for the definition with the phase-space density ω into one for the definition with the phase-space volume Ω, the correspondence is

$$\Omega_{mn} \to \Omega_{m-1,n}\Omega_{00}^{-1}, \tag{16}$$

with the special case $\Omega_{20} \to \Omega_{00}^{-1}$ since $\Omega_{10} = 1$. Equation (16) can readily be obtained by replacing m by $m - 1$ in the correspondence $\Omega_{00}^{-1}\Omega_{mn} \leftrightarrow \Omega_{m+1,n}$ described above.

The total differential of the entropy $S = S(N, p, H)$ reads [2]

$$\mathrm{d}S = \frac{1}{T}\mathrm{d}H - \frac{V}{T}\mathrm{d}p - \frac{\mu}{T}\mathrm{d}N. \tag{17}$$

Since the NpH ensemble describes closed systems, $\mathrm{d}N = 0$. The total differential provides the starting point for the derivation of expressions for thermodynamic properties in terms of phase-space functions. The inverse temperature is the derivative of the entropy with respect to enthalpy:

$$\frac{1}{T} = \left(\frac{\partial S}{\partial H}\right)_p = k_\mathrm{B}\mathcal{S}_{10} \overset{\Omega}{=} k_\mathrm{B}\Omega_{00}^{-1}. \tag{18}$$

Thus, the expression for the temperature reads

$$T \overset{\Omega}{=} k_\mathrm{B}^{-1}\Omega_{00}. \tag{19}$$

Similarly, the expression for the volume,

$$V = -T\left(\frac{\partial S}{\partial p}\right)_H \overset{\Omega}{=} -\frac{\Omega_{00}}{k_\mathrm{B}}k_\mathrm{B}\mathcal{S}_{01} = -\Omega_{01}, \tag{20}$$

is found. The corresponding expressions for the entropy definition in terms of the phase-space density, Eq. (4), are obtained as

$$T \overset{\omega}{=} k_\mathrm{B}^{-1}\Omega_{20}^{-1}, \tag{21}$$

$$V \overset{\omega}{=} -\Omega_{11}\Omega_{20}^{-1}, \tag{22}$$

using the correspondence given by Eq. (15). At this point, it is instructive to derive expressions for the derivatives of temperature and volume with respect to enthalpy and pressure for both entropy definitions as they are required in the derivation of expressions for thermodynamic properties, which are related to second-order derivatives of the entropy. They are found by applying the recursion relations, Eqs. (9) and (10), on Eqs. (19)–(22). The results are reported in Table II.

With these preparations, expressions for further thermodynamic properties can be established. In the following, this procedure is elaborated for the definition of the entropy in terms of the phase-space volume, Eq. (3). The expression for the isobaric heat capacity, $C_p = (\partial H/\partial T)_p$, is obtained by using the expression for the derivative $(\partial T/\partial H)_p$ from Table II as

$$C_p = \left(\frac{\partial H}{\partial T}\right)_p = \left(\frac{\partial T}{\partial H}\right)_p^{-1} \overset{\Omega}{=} k_\mathrm{B}(1 - \Omega_{00}\Omega_{20})^{-1}. \tag{23}$$

Analogously, the expression for the thermal expansion coefficient $\alpha_p = V^{-1}(\partial V/\partial T)_p$ can be found. A thermodynamic transformation of the defining equation yields

$$\alpha_p = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p = \frac{1}{V}\left(\frac{\partial V}{\partial H}\right)_p\left(\frac{\partial H}{\partial T}\right)_p = \frac{C_p}{V}\left(\frac{\partial V}{\partial H}\right)_p. \tag{24}$$

Inserting Eq. (23) for the isobaric heat capacity, Eq. (20) for the volume, and the expression for the derivative $(\partial V/\partial H)_p$ from Table II leads to

$$\alpha_p \overset{\Omega}{=} \frac{k_\mathrm{B}(\Omega_{11} - \Omega_{20}\Omega_{01})}{\Omega_{01}(1 - \Omega_{00}\Omega_{20})}. \tag{25}$$

The expression for the Joule-Thomson coefficient μ_JT can straightforwardly be found in the NpH ensemble. It is given

TABLE II. Expressions for derivatives of the temperature and volume in terms of phase-space functions Ω_{mn} for both entropy definitions.

	$S \overset{\Omega}{=} k_\mathrm{B} \ln \Omega$	$S \overset{\omega}{=} k_\mathrm{B} \ln \omega$
$\left(\frac{\partial T}{\partial H}\right)_p$	$k_\mathrm{B}^{-1}(1 - \Omega_{20}\Omega_{00})$	$k_\mathrm{B}^{-1}\left(1 - \Omega_{30}\Omega_{20}^{-2}\right)$
$\left(\frac{\partial T}{\partial p}\right)_H$	$k_\mathrm{B}^{-1}(\Omega_{01} - \Omega_{11}\Omega_{00})$	$k_\mathrm{B}^{-1}\Omega_{20}^{-1}\left(\Omega_{11} - \Omega_{21}\Omega_{20}^{-1}\right)$
$\left(\frac{\partial V}{\partial H}\right)_p$	$\Omega_{20}\Omega_{01} - \Omega_{11}$	$\Omega_{20}^{-1}\left(\Omega_{30}\Omega_{11}\Omega_{20}^{-1} - \Omega_{21}\right)$
$\left(\frac{\partial V}{\partial p}\right)_H$	$\Omega_{11}\Omega_{01} - \Omega_{02}$	$\Omega_{20}^{-1}\left(\Omega_{21}\Omega_{11}\Omega_{20}^{-1} - \Omega_{12}\right)$

by

$$\mu_{\mathrm{JT}} = \left(\frac{\partial T}{\partial p}\right)_H \overset{\Omega}{=} k_{\mathrm{B}}^{-1}(\Omega_{01} - \Omega_{00}\Omega_{11}). \tag{26}$$

Next, the expression for the isothermal compressibility,

$$\beta_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T, \tag{27}$$

is derived. Since the temperature is not an independent variable in the NpH ensemble, the derivative $(\partial V/\partial p)_T$ must be transformed into derivatives with respect to enthalpy and pressure. This is achieved by the method using Jacobian determinants as described by Münster [53], which was also applied to transform derivatives in the development of the theory for other ensembles [33–35]. Applying this method to the derivative $(\partial V/\partial p)_T$ leads to

$$\left(\frac{\partial V}{\partial p}\right)_T \equiv \frac{\partial(V,T)}{\partial(p,T)} = \frac{\frac{\partial(V,T)}{\partial(H,p)}}{\frac{\partial(p,T)}{\partial(H,p)}} \equiv \frac{\begin{vmatrix} \left(\frac{\partial V}{\partial H}\right)_p & \left(\frac{\partial V}{\partial p}\right)_H \\ \left(\frac{\partial T}{\partial H}\right)_p & \left(\frac{\partial T}{\partial p}\right)_H \end{vmatrix}}{\begin{vmatrix} \left(\frac{\partial p}{\partial H}\right)_p & \left(\frac{\partial p}{\partial p}\right)_H \\ \left(\frac{\partial T}{\partial H}\right)_p & \left(\frac{\partial T}{\partial p}\right)_H \end{vmatrix}}$$

$$= \left(\frac{\partial V}{\partial p}\right)_H - \left(\frac{\partial V}{\partial H}\right)_p \frac{\left(\frac{\partial T}{\partial p}\right)_H}{\left(\frac{\partial T}{\partial H}\right)_p}, \tag{28}$$

where the determinant in the denominator simplifies because $(\partial p/\partial H)_p = 0$ and $(\partial p/\partial p)_H = 1$. Finally, the partial derivatives in Eq. (28) are replaced by the expressions in Table II, which yields

$$\beta_T \overset{\Omega}{=} \Omega_{11} - \frac{\Omega_{02}}{\Omega_{01}} - \left(\Omega_{20} - \frac{\Omega_{11}}{\Omega_{01}}\right)\frac{\Omega_{01} - \Omega_{00}\Omega_{11}}{1 - \Omega_{00}\Omega_{20}}. \tag{29}$$

In the same way, the expression for the thermal pressure coefficient $\gamma_V = (\partial p/\partial T)_V$ is derived. The derivative $(\partial p/\partial T)_V$ is transformed by the method using Jacobian determinants, which results in

$$\left(\frac{\partial p}{\partial T}\right)_V \equiv \frac{\partial(p,V)}{\partial(T,V)} = \frac{\frac{\partial(p,V)}{\partial(H,p)}}{\frac{\partial(T,V)}{\partial(H,p)}} \equiv \frac{\begin{vmatrix} \left(\frac{\partial p}{\partial H}\right)_p & \left(\frac{\partial p}{\partial p}\right)_H \\ \left(\frac{\partial V}{\partial H}\right)_p & \left(\frac{\partial V}{\partial p}\right)_H \end{vmatrix}}{\begin{vmatrix} \left(\frac{\partial T}{\partial H}\right)_p & \left(\frac{\partial T}{\partial p}\right)_H \\ \left(\frac{\partial V}{\partial H}\right)_p & \left(\frac{\partial V}{\partial p}\right)_H \end{vmatrix}}$$

$$= -\frac{\left(\frac{\partial V}{\partial H}\right)_p}{\left(\frac{\partial T}{\partial H}\right)_p\left(\frac{\partial V}{\partial p}\right)_H - \left(\frac{\partial V}{\partial H}\right)_p\left(\frac{\partial T}{\partial p}\right)_H}. \tag{30}$$

The expression for the thermal pressure coefficient follows as

$$\gamma_V \overset{\Omega}{=} \frac{k_{\mathrm{B}}(\Omega_{11} - \Omega_{20}\Omega_{01})}{(1 - \Omega_{00}\Omega_{20})(\Omega_{11}\Omega_{01} - \Omega_{02}) + (\Omega_{01} - \Omega_{00}\Omega_{11})(\Omega_{11} - \Omega_{20}\Omega_{01})}. \tag{31}$$

Further thermodynamic properties, such as the isochoric heat capacity or speed of sound, can be calculated from the isobaric heat capacity, the thermal expansion coefficient, the Joule-Thomson coefficient, the isothermal compressibility, and the thermal pressure coefficient by well-known thermodynamic relations [53]. The expressions for the entropy definition in terms of the phase-space density are obtained from those for the entropy definition in terms of the phase-space volume using the correspondence given by Eq. (15). Table III summarizes the expressions for all considered thermodynamic properties in terms of phase-space functions for both entropy definitions.

In the second step, the phase-space functions are related to ensemble averages, which in the NpH ensemble comprise combinations of instantaneous values of the kinetic energy $K = H - U - pV$ and volume V. Here, we consider only systems of pure fluids, which consist of spherical particles with three translational degrees of freedom. The corresponding results for the thermodynamic properties of systems of particles with additional rotational degrees of freedom are readily obtained by replacing $3N$ in all equations in the remainder of this article by the total number of degrees of freedom, fN, where f is the number of degrees of freedom of one molecule.

Provided that the potential energy is only a function of the particle coordinates, the internal energy $E = K + U$ can be separated into the kinetic energy $K = \sum \mathbf{p}_i^2/2m$ and the potential energy U. The integrals over the momenta of the particles in the phase-space volume are evaluated using the Laplace-transform technique by Pearson *et al.* [7]. Applying the Laplace transform with respect to enthalpy on the phase-space volume, Eq. (1), yields

$$\mathscr{L}_H(\Omega) = \frac{1}{N!h^{3N}}\int_0^\infty \iint \frac{N}{V}\frac{1}{s}\exp\left[-s\left(\sum_{i=1}^N \mathbf{p}_i^2/2m + U + pV\right)\right]d\mathbf{r}^N d\mathbf{p}^N dV, \tag{32}$$

where s is the Laplace variable and the $3N$ integrals over the momenta are integrals over Gaussian exponential functions, which can readily be evaluated. This yields

$$\mathscr{L}_H(\Omega) = \frac{(2\pi m)^{3N/2}}{N!h^{3N}}\int_0^\infty \int \frac{N}{V}\left(\frac{1}{s}\right)^{3N/2+1} \times \exp[-s(U + pV)]d\mathbf{r}^N dV. \tag{33}$$

Applying the inverse Laplace transform results in

$$\Omega = C\left(\frac{3N}{2}\right)^{-1}\int_0^\infty \int V^{-1}(H - U - pV)^{3N/2} \times \Theta(H - U - pV)d\mathbf{r}^N dV, \tag{34}$$

in which the abbreviation

$$C = \frac{N}{N!\,h^{3N}}\frac{(2\pi m)^{3N/2}}{\Gamma(3N/2)} \tag{35}$$

has been introduced. $\Gamma(x)$ denotes the gamma function, for which the recurrence relation $\Gamma(x+1) = x\Gamma(x)$ holds

TABLE III. Relations for important thermodynamic properties in terms of phase-space functions Ω_{mn} derived from both entropy definitions $S \overset{\Omega}{=} k_\mathrm{B} \ln \Omega$ and $S \overset{\omega}{=} k_\mathrm{B} \ln \omega$. In the expressions for the speed of sound, M denotes the molar mass.

	$S \overset{\Omega}{=} k_\mathrm{B} \ln \Omega$
Isobaric heat capacity	$C_p = \left(\frac{\partial H}{\partial T}\right)_p \overset{\Omega}{=} k_\mathrm{B}(1 - \Omega_{00}\Omega_{20})^{-1}$
Isochoric heat capacity	$C_V = \left(\frac{\partial E}{\partial T}\right)_V \overset{\Omega}{=} k_\mathrm{B}(1 - \Omega_{00}\Omega_{20})^{-1} \times \left[1 + \frac{\Omega_{00}(\Omega_{11} - \Omega_{20}\Omega_{01})^2}{(1 - \Omega_{00}\Omega_{20})(\Omega_{11}\Omega_{01} - \Omega_{02}) - (\Omega_{01} - \Omega_{00}\Omega_{11})(\Omega_{20}\Omega_{01} - \Omega_{11})}\right]$
Thermal expansion coefficient	$\alpha_p = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p \overset{\Omega}{=} \frac{k_\mathrm{B}(\Omega_{11} - \Omega_{20}\Omega_{01})}{\Omega_{01}(1 - \Omega_{00}\Omega_{20})}$
Isothermal compressibility	$\beta_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T \overset{\Omega}{=} \Omega_{11} - \frac{\Omega_{02}}{\Omega_{01}} - \left(\Omega_{20} - \frac{\Omega_{11}}{\Omega_{01}}\right)\frac{\Omega_{01} - \Omega_{00}\Omega_{11}}{1 - \Omega_{00}\Omega_{20}}$
Thermal pressure coefficient	$\gamma_V = \left(\frac{\partial p}{\partial T}\right)_V \overset{\Omega}{=} \frac{k_\mathrm{B}(\Omega_{11} - \Omega_{20}\Omega_{01})}{(1 - \Omega_{00}\Omega_{20})(\Omega_{11}\Omega_{01} - \Omega_{02}) - (\Omega_{01} - \Omega_{00}\Omega_{11})(\Omega_{20}\Omega_{01} - \Omega_{11})}$
Isentropic compressibility	$\beta_S = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_S = \beta_T \frac{C_V}{C_p} \overset{\Omega}{=} 2\Omega_{11} - \Omega_{20}\Omega_{01} - \frac{\Omega_{02}}{\Omega_{01}}$
Speed of sound	$w^2 = -\frac{V^2}{NM}\left(\frac{\partial p}{\partial V}\right)_S = \frac{V}{NM\beta_S} \overset{\Omega}{=} \frac{1}{NM}\frac{\Omega_{01}^2}{\Omega_{02} + \Omega_{20}\Omega_{01}^2 - 2\Omega_{11}\Omega_{01}}$
Joule-Thomson coefficient	$\mu_\mathrm{JT} = \left(\frac{\partial T}{\partial p}\right)_H \overset{\Omega}{=} k_\mathrm{B}^{-1}(\Omega_{01} - \Omega_{00}\Omega_{11})$
	$S \overset{\omega}{=} k_\mathrm{B} \ln \omega$
Isobaric heat capacity	$C_p = \left(\frac{\partial H}{\partial T}\right)_p \overset{\omega}{=} k_\mathrm{B}\big(1 - \Omega_{30}\Omega_{20}^{-2}\big)^{-1}$
Isochoric heat capacity	$C_V = \left(\frac{\partial E}{\partial T}\right)_V \overset{\omega}{=} k_\mathrm{B}\big(1 - \Omega_{30}\Omega_{20}^{-2}\big)^{-1} \times \left[1 + \frac{(\Omega_{21}\Omega_{20} - \Omega_{30}\Omega_{11})^2}{\big(\Omega_{20}^3 - \Omega_{30}\Omega_{20}\big)(\Omega_{21}\Omega_{11} - \Omega_{12}\Omega_{20}) - (\Omega_{11}\Omega_{20} - \Omega_{21})(\Omega_{30}\Omega_{11}\Omega_{20} - \Omega_{21}\Omega_{20}^2)}\right]$
Thermal expansion coefficient	$\alpha_p = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p \overset{\omega}{=} \frac{k_\mathrm{B}(\Omega_{21} - \Omega_{30}\Omega_{11}\Omega_{20}^{-1})}{\Omega_{11}(1 - \Omega_{30}\Omega_{20}^{-2})}$
Isothermal compressibility	$\beta_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T \overset{\omega}{=} \frac{\Omega_{21}}{\Omega_{20}} - \frac{\Omega_{12}}{\Omega_{11}} - \left(\frac{\Omega_{30}}{\Omega_{20}} - \frac{\Omega_{21}}{\Omega_{11}}\right)\frac{\Omega_{11}\Omega_{20} - \Omega_{21}}{\Omega_{20}^2 - \Omega_{30}}$
Thermal pressure coefficient	$\gamma_V = \left(\frac{\partial p}{\partial T}\right)_V \overset{\omega}{=} \frac{k_\mathrm{B}(\Omega_{21}\Omega_{20} - \Omega_{30}\Omega_{11})}{(1 - \Omega_{30}\Omega_{20}^{-2})(\Omega_{21}\Omega_{11} - \Omega_{12}\Omega_{20}) - (\Omega_{11}\Omega_{20} - \Omega_{21})(\Omega_{30}\Omega_{11}\Omega_{20}^{-2} - \Omega_{21}\Omega_{20}^{-1})}$
Isentropic compressibility	$\beta_S = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_S = \beta_T \frac{C_V}{C_p} \overset{\omega}{=} \frac{2\Omega_{21}}{\Omega_{20}} - \frac{\Omega_{30}\Omega_{11}}{\Omega_{20}^2} - \frac{\Omega_{12}}{\Omega_{11}}$
Speed of sound	$w^2 = -\frac{V^2}{NM}\left(\frac{\partial p}{\partial V}\right)_S = \frac{V}{NM\beta_S} \overset{\omega}{=} \frac{\Omega_{11}^2\Omega_{20}}{NM(\Omega_{12}\Omega_{20}^2 + \Omega_{30}\Omega_{11}^2 - 2\Omega_{21}\Omega_{11}\Omega_{20})}$
Joule-Thomson coefficient	$\mu_\mathrm{JT} = \left(\frac{\partial T}{\partial p}\right)_H \overset{\omega}{=} k_\mathrm{B}^{-1}\big(\Omega_{11}\Omega_{20}^{-1} - \Omega_{21}\Omega_{20}^{-2}\big)$

[54]. Analogously, the integrals over the momenta in the phase-space density can be evaluated to obtain

$$\omega = C \int_0^\infty \int V^{-1}(H - U - pV)^{3N/2-1} \times \Theta(H - U - pV)\, d\mathbf{r}^N dV, \tag{36}$$

and the ensemble average of an arbitrary property A is defined by

$$\langle A \rangle = \frac{C}{\omega} \int_0^\infty \int A\, V^{-1}(H - U - pV)^{3N/2-1} \times \Theta(H - U - pV)\, d\mathbf{r}^N dV. \tag{37}$$

TABLE IV. Explicit expressions for phase-space functions Ω_{mn} up to third order in the *NpH* ensemble.

$$\Omega_{00} = \left(\tfrac{3N}{2}\right)^{-1}\langle H - U - pV\rangle$$
$$\Omega_{10} = 1$$
$$\Omega_{20} = \left(\tfrac{3N}{2} - 1\right)\langle (H - U - pV)^{-1}\rangle$$
$$\Omega_{30} = \left(\tfrac{3N}{2} - 1\right)\left(\tfrac{3N}{2} - 2\right)\langle (H - U - pV)^{-2}\rangle$$
$$\Omega_{01} = -\langle V\rangle$$
$$\Omega_{02} = \left(\tfrac{3N}{2} - 1\right)\langle (H - U - pV)^{-1}V^2\rangle$$
$$\Omega_{03} = \left(1 - \tfrac{3N}{2}\right)\left(\tfrac{3N}{2} - 2\right)\langle (H - U - pV)^{-2}V^3\rangle$$
$$\Omega_{11} = \left(1 - \tfrac{3N}{2}\right)\langle (H - U - pV)^{-1}V\rangle$$
$$\Omega_{12} = \left(\tfrac{3N}{2} - 1\right)\left(\tfrac{3N}{2} - 2\right)\langle (H - U - pV)^{-2}V^2\rangle$$
$$\Omega_{21} = \left(1 - \tfrac{3N}{2}\right)\left(\tfrac{3N}{2} - 2\right)\langle (H - U - pV)^{-2}V\rangle$$

A comparison of Eqs. (36) and (37) shows that the constant C cancels and, thus, is not required to calculate ensemble averages. With these preparations, the expressions for the phase-space functions in terms of ensemble averages can be established. A phase-space function $\Omega_{mn} = \omega^{-1}\partial^{m+n}\Omega/\partial^m H\partial^n p$ is defined as the product of the inverse phase-space density and a derivative of the phase-space volume. Thus, an expression in terms of ensemble averages can be found by calculating the derivative of the phase-space volume, Eq. (34), dividing it by the phase-space density, and comparing the result with the general equation for an ensemble average, Eq. (37). For instance, the expression for $\Omega_{00} = \Omega/\omega$ is obtained by using Eq. (34) as

$$\begin{aligned}\Omega_{00} = &\frac{C}{\omega}\left(\frac{3N}{2}\right)^{-1}\int_0^\infty\int V^{-1}(H - U - pV)^{3N/2}\\ &\times\Theta(H - U - pV)d\mathbf{r}^N dV\\ = &\left(\frac{3N}{2}\right)^{-1}\langle H - U - pV\rangle,\end{aligned}\tag{38}$$

and the expression for the phase-space function $\Omega_{01} = \omega^{-1}\partial\Omega/\partial p$ is found as

$$\begin{aligned}\Omega_{01} = &\frac{C}{\omega}\left(\frac{3N}{2}\right)^{-1}\int_0^\infty\int V^{-1}\frac{3N}{2}\\ &\times(H - U - pV)^{3N/2-1}(-V)\\ &\times\Theta(H - U - pV)d\mathbf{r}^N dV = -\langle V\rangle.\end{aligned}\tag{39}$$

Continuing this procedure, expressions for phase-space functions of higher order can be obtained. The results for all phase-space functions up to third order are listed in Table IV.

By mathematical induction, the general expression

$$\Omega_{mn} = \mathcal{P}_{m+n}^{-3N/2}\left\langle\left(\frac{H - U - pV}{3N/2}\right)^{1-m-n}(-V)^n\right\rangle\tag{40}$$

for phase-space functions of arbitrary order can be established, in which the symbol $\mathcal{P}_x^X$ denotes the Pochhammer polynomials [54]:

$$\mathcal{P}_x^X = \begin{cases}1 & \text{for x = 0 or x = 1}\\ \left(1 + \dfrac{1}{X}\right)\cdots\left(1 + \dfrac{x-1}{X}\right) & \text{otherwise.}\end{cases}\tag{41}$$

They account for the factors that arise from the exponent of the kinetic energy in the phase-space volume with each order of derivative. Note that, since $K = H - U - pV > 0$, the first factor in the angular brackets in Eq. (40) always remains finite.

As in the isothermal-isobaric ensemble, the expressions for the phase-space functions do not contain volume derivatives of the potential energy, but only combinations of the kinetic energy and volume. Since these terms can readily be calculated in a simulation, this is a computational advantage compared to ensembles in which the volume is an independent variable, such as the microcanonical and canonical ensembles, where additionally volume derivatives of the potential energy appear in the expressions for the phase-space functions.

When the expressions for the phase-space functions in Table IV are inserted into the equations for the thermodynamic properties presented in Table III, expressions for the properties in terms of ensemble averages are obtained. The equations for the isobaric heat capacity,

$$C_p \overset{\Omega}{=} k_\mathrm{B}\left[1 - \left(1 - \frac{2}{3N}\right)\langle K\rangle\langle K^{-1}\rangle\right]^{-1},\tag{42}$$

thermal pressure coefficient,

$$\alpha_p \overset{\Omega}{=} k_\mathrm{B}\frac{(3N/2 - 1)(\langle K^{-1}V\rangle - \langle K^{-1}\rangle\langle V\rangle)}{\langle V\rangle[1 - (1 - 2/3N)\langle K\rangle\langle K^{-1}\rangle]},\tag{43}$$

and isentropic compressibility,

$$\beta_S \overset{\Omega}{=} \left(\frac{3N}{2} - 1\right)\left(\langle K^{-1}\rangle\langle V\rangle - 2\langle K^{-1}V\rangle + \frac{\langle K^{-1}V^2\rangle}{\langle V\rangle}\right),\tag{44}$$

for the entropy definition with the phase-space volume, Eq. (3), agree with those derived by Ray and Graben [8]. The equations for the isochoric heat capacity, isothermal compressibility, speed of sound, and Joule-Thomson coefficient for the entropy definition with the phase-space volume in Table III, the equations for all properties for the entropy definition with the phase-space density in Table III, and for the third-order derivatives of the entropy in Table I have not yet been reported in the literature. Beyond that, the Lustig methodology enables to derive equations for derivatives of the entropy of arbitrary order by using the recursion formulas, Eqs. (9) and (10), and the general equation for the phase-space functions, Eq. (40).

The implementation of the derived expressions in a Monte Carlo code is straightforward. During the production phase of a simulation, the instantaneous values for the ensemble averages, which appear in the phase-space functions, must be accumulated. After the production phase has been finished, ensemble averages are formed, and the phase-space functions using the equations in Table IV and with them the derivatives of the entropy and thermodynamic properties using the equations in Tables I and III are calculated. Alternatively, the phase-space functions can also be calculated by the general equation, Eq. (40).

III. VALIDATION BY MONTE CARLO SIMULATIONS OF A MODEL FLUID

The expressions derived in Sec. II were validated by Monte Carlo simulations of the simple Lennard-Jones model fluid as a test case. In general, the probability P_{mn} to accept a Monte Carlo move from the old state m to the new state n of a Markov chain generated by the Metropolis algorithm [55] is determined by

$$P_{mn} = \min\left(1, \frac{W_n}{W_m}\right), \tag{45}$$

where W is the weight factor of the ensemble. In the NpH ensemble, the Markov chain consists of two different types of trials, particle displacements and volume changes. An acceptance criterion for particle displacements in Monte Carlo simulations of the microcanonical ensemble was described by Ray [56] and Lustig [31]. The weight factor can be inferred from the phase-space density of the microcanonical ensemble,

$$\omega_{NVE} = C_{NVE} \int (E-U)^{3N/2-1}\Theta(E-U)d\mathbf{r}^N, \tag{46}$$

with

$$C_{NVE} = \frac{1}{N!h^{3N}}\frac{(2\pi m)^{3N/2}}{\Gamma(3N/2)} \tag{47}$$

and is given by

$$W_{NVE} = (E-U)^{3N/2-1}\Theta(E-U). \tag{48}$$

Since the NpH ensemble is also an adiabatic ensemble, the weight factor can be derived from the phase-space density, Eq. (36), in the same way. In order to show the volume dependence of the integrand in Eq. (36) explicitly, dimensionless coordinates $\mathbf{r}'_i = \mathbf{r}_i V^{-1/3}$ are introduced, which results in

$$\omega = C\int_0^\infty \int (H-U-pV)^{3N/2-1}V^{N-1} \times \Theta(H-U-pV)d\mathbf{r}'^N dV. \tag{49}$$

Thus, the weight factor of the NpH ensemble is given by

$$W_{NpH} = (H-U-pV)^{3N/2-1}\Theta(H-U-pV)V^{N-1}, \tag{50}$$

and the acceptance criterion for a particle displacement or volume change in the NpH ensemble is obtained as

$$P_{mn} = \min\left[1, \left(\frac{H-U_n-pV_n}{H-U_m-pV_m}\right)^{3N/2-1} \times \frac{\Theta(H-U_n-pV_n)}{\Theta(H-U_m-pV_m)}\left(\frac{V_n}{V_m}\right)^{N-1}\right], \tag{51}$$

where the factor $(V_n/V_m)^{N-1}$ arises from the volume dependence of the particle coordinates and the volume scale, which was introduced in Eq. (2).

The Metropolis algorithm for the NpH ensemble was implemented into the FORTRAN 90 software developed in our previous work on the NpT and grand canonical ensembles [34,35]. This software is based on FORTRAN 77 code segments published as attachments to the book of Allen and Tildesley [57].

The Markov chain was divided into cycles, where each cycle consisted of N trials. In order to ensure that detailed balance is fulfilled, the type of trial at each step of the Markov chain was selected randomly by the following procedure. Whether a particle displacement or volume change was attempted was determined by a random number ξ_1 uniformly distributed in the interval [0,1]. If $\xi_1 < 1/N$, a volume change, otherwise a particle displacement was attempted. If a particle displacement was chosen, a second random number ξ_2 from a uniform distribution in [0,1] was generated. The number of the particle to be displaced was then determined by $\mathrm{int}(N\xi_2)+1$. Throughout the simulation, the random number generator `ran2` published by Press *et al.* [58] was used.

In this work, the usual Lennard-Jones dimensionless quantity system is used. All properties are reduced by the length parameter σ and well depth ε of the Lennard-Jones potential

$$u(r) = 4\,\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]. \tag{52}$$

The reduced quantities are defined by $T^* = Tk_\mathrm{B}/\varepsilon$, $p^* = p\sigma^3/\varepsilon$, $\rho^* = \rho\sigma^3$, $E^* = E/\varepsilon$, $H^* = H/\varepsilon$, $C_V^* = C_V/k_\mathrm{B}$, $C_p^* = C_p/k_\mathrm{B}$, $\gamma_\mathrm{V}^* = \gamma_\mathrm{V}\sigma^3/k_\mathrm{B}$, $\alpha_p^* = \alpha_p k_\mathrm{B}/\varepsilon$, $\beta_T^* = \beta_T\sigma^3/\varepsilon$, $\beta_S^* = \beta_S\sigma^3/\varepsilon$, $w^* = w(NM/\varepsilon)^{1/2}$, and $\mu_\mathrm{JT}^* = \mu_\mathrm{JT}k_\mathrm{B}/\sigma^3$, where M denotes the molar mass. Since only reduced quantities will be discussed in the remainder of this section, the asterisks are omitted for brevity in the following.

The state points ($p = 0.05$, $h = 2.5$) in the gas region, ($p = 1.0$, $h = -2.5$) in the liquid region, and ($p = 3.0$, $h = 10.0$) in the supercritical region were chosen for the validation, where $h = H/N$ denotes the enthalpy per particle. With this choice, three characteristic states in the fluid region are simulated. Since we are interested in thermodynamic properties of macroscopic systems in the thermodynamic limit, at each state point eight simulations were carried out with 64, 108, 128, 216, 256, 500, 864, and 1372 particles, and the results of these simulations were extrapolated into the thermodynamic limit $N \to \infty$. By this means, systematic errors in the results for thermodynamic properties due to the use of finite numbers of particles are eliminated.

Depending on the number of particles, the simulations were started from different lattice configurations. For 108, 256, 500, 864, and 1372 particles, a face-centered cubic lattice was chosen. The simulations with 128 particles were started from a body-centered cubic lattice, while those with 64 and 216 particles used a simple cubic lattice as the start configuration. Each simulation was preceded by an equilibration phase over 10^5 cycles. After that, the production phase comprised 10^7 cycles. In all simulations, the cutoff radius was set to half of the box length. To account for interactions between pairs of particles whose distance is larger than the cutoff radius, the long-range correction for the potential energy was calculated as described by Allen and Tildesley [57]. When the volume was changed, both cutoff radius and long-range correction were adapted.

During the production phase of the simulation, instantaneous values for all ensemble averages required to calculate the phase-space functions in Table IV were accumulated at the end of each cycle. After the production phase had been completed, ensemble averages and phase-space functions were

TABLE V. Monte Carlo simulation results, their expanded uncertainty (at the 0.95 confidence level), and values calculated with the equation of state of Thol *et al.* [37] for several thermodynamic properties at three state points of the Lennard-Jones model fluid using both definition $S \overset{\Omega}{=} k_\mathrm{B} \ln \Omega$ and $S \overset{\omega}{=} k_\mathrm{B} \ln \omega$. Each simulation comprised 10^7 cycles. The simulations were carried out with 64, 108, 128, 216, 256, 500, 864, and 1372 particles. The values reported are extrapolated values in the thermodynamic limit $N \to \infty$. The values of the equation of state were calculated with the prescribed pressure and the extrapolated value of the temperature. Expanded uncertainties are given by the numbers in parentheses; i.e., 3.664(8) means that the value 3.664 has an expanded uncertainty of 0.008.

	Gas $p = 0.05, h = 2.5$		Liquid $p = 1.0, h = -2.5$		Supercritical $p = 3.0, h = 10.0$	
Property	Simulation	EOS	Simulation	EOS	Simulation	EOS
			$S \overset{\Omega}{=} k_\mathrm{B} \ln \Omega$			
T	1.242767(49)	1.242804	1.05781(7)	1.05781	3.97516(14)	3.97520
ρ	0.0483424(23)	0.0483438	0.780391(13)	0.779970	0.463152(11)	0.463121
E/N	1.46572(5)	1.46599	−3.781416(21)	−3.777798	3.52265(16)	3.52165
C_V/N	1.68018(45)	1.6763	2.3213(15)	2.3139	1.72209(21)	1.72382
C_p/N	3.664(8)	3.647	4.820(21)	4.787	3.247(6)	3.249
γ_V	0.055701(13)	0.05564	4.450(7)	4.445	1.01101(48)	1.0107
α_p	1.386(5)	1.378	0.4139(27)	0.410	0.1758(7)	0.1758
β_T	24.88(9)	24.76	0.09301(49)	0.0923	0.1739(6)	0.1740
β_S	11.407(19)	11.382	0.04480(8)	0.044623	0.09220(15)	0.09230
w	1.3466(11)	1.3481	5.3480(46)	5.360	4.8391(40)	4.837
μ_JT	4.076(29)	4.041	−0.1493(14)	−0.1516	−0.2003(21)	−0.2001
			$S \overset{\omega}{=} k_\mathrm{B} \ln \omega$			
T	1.242763(49)	1.24280	1.05784(7)	1.05784	3.97516(14)	3.97520
ρ	0.0483430(23)	0.0483441	0.780390(13)	0.779960	0.463152(11)	0.463121
E/N	1.46572(5)	1.46598	−3.781423(21)	−3.777664	3.52265(15)	3.52163
C_V/N	1.68017(45)	1.6763	2.3216(15)	2.3139	1.72209(21)	1.72382
C_p/N	3.664(8)	3.647	4.822(21)	4.787	3.247(6)	3.249
γ_V	0.055700(31)	0.05564	4.451(7)	4.444	1.01101(48)	1.0107
α_p	1.386(5)	1.378	0.4141(27)	0.410	0.1758(7)	0.1758
β_T	24.88(9)	24.76	0.0930(5)	0.0923	0.1739(6)	0.1740
β_S	11.407(19)	11.382	0.04480(8)	0.04462	0.09220(15)	0.09230
w	1.3467(23)	1.3481	5.3479(46)	5.360	4.8391(40)	4.837
μ_JT	4.077(29)	4.041	−0.1492(14)	−0.1516	−0.2003(21)	−0.2001

calculated. Values for the thermodynamic properties for both entropy definitions were obtained by using the relations reported in Table III. The uncertainty of the simulation results was estimated by the method of statistical inefficiency as recommended by Allen and Tildesley [57], which is originally due to Friedberg and Cameron [59]. This method requires instantaneous values for all thermodynamic properties. Since it is not possible to calculate instantaneous values of properties related to second-order derivatives of the entropy, such as the heat capacities or compressibilities, the method proposed by Lustig [27] was applied to estimate instantaneous values for these properties.

The extrapolation of the results into the thermodynamic limit was carried out by a weighted linear least-squares fit to the results for each property as a function of the inverse number of particles. The inverse variance of each property was used as weight. The uncertainty of the extrapolated values was estimated by the Monte Carlo method described in the "Guide to the Expression of Uncertainty in Measurement" (GUM) [60]. In this method, a Monte Carlo trial consists of a weighted linear least-squares fit to randomly disturbed simulation results as a function of the inverse number of particles. The random disturbances are determined from a Gaussian distribution with the standard deviation equal to the standard uncertainty of the simulation result. The number of trials was set to $M = 10^6$ as proposed in the GUM [60]. The average of the extrapolated values of all trials was then taken as the result for the property in the thermodynamic limit and the standard deviation as its standard uncertainty. At the liquid state ($p = 1.0$, $h = -2.5$), the values for 64 particles for most properties deviate significantly from the linear behavior as a function of the inverse number of particles. This is probably due to the high density of the state point, where a small cutoff radius has to be chosen. Therefore, the results for 64 particles were not used in the extrapolation at this state.

The results for the properties in the thermodynamic limit and their uncertainties (at the 0.95 confidence level) for both entropy definitions are reported in Table V. With the extrapolated values for the temperature and the prescribed pressure, values for each property were calculated with the reference equation of state (EOS) by Thol *et al.* [37], which has been shown by Stephan *et al.* [61] to be among the most accurate representations of the properties of the Lennard-Jones model fluid. These values are also reported in Table V. According to Thol *et al.* [37], the uncertainty of densities calculated with the EOS amounts to 0.1% in the liquid region, 1.0% in the gas region, and 0.15% to 0.3% in the supercritical region. For other properties, it is 0.5% in the isochoric heat capacity, 1.0%

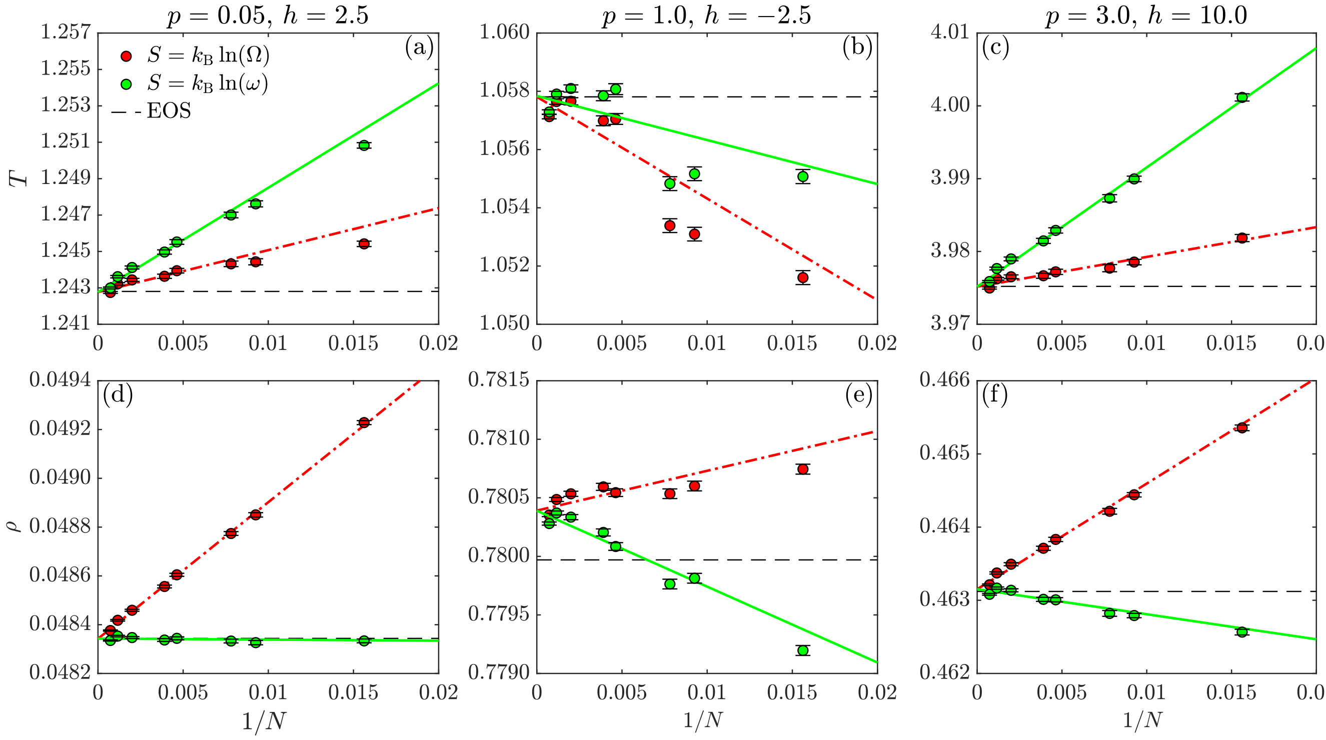

FIG. 1. (a–f) Results of the Monte Carlo simulations for the temperature and density at three state points of the Lennard-Jones model fluid as a function of the inverse number of particles. The solid green and dash-dotted red lines represent weighted linear least-squares fits to the data, the error bars show the uncertainty in the simulation results, and the dashed black lines represent values calculated with the EOS of Thol *et al.* [37].

in the isobaric heat capacity, speed of sound, and thermal pressure coefficient, 3.0% in the isothermal compressibility, 2.5–10 % in the Joule-Thomson coefficient, and 15% in the thermal expansion coefficient.

The results for the temperature and density, which correspond to first-order derivatives of the entropy, are shown in Fig. 1 as a function of the inverse number of particles. Also included as green and red lines are the results of the weighted linear least-squares fits to the simulation results. In most cases, both properties exhibit a strong dependence on the number of particles. Thus, in order to obtain results that correspond to properties of macroscopic systems, very large systems must be simulated or results obtained from simulations of small systems must be extrapolated to the thermodynamic limit. At the gas and supercritical state, the results for different system sizes agree mostly with the linear fit within their uncertainty. In the liquid region, the results show larger deviations from the fit function than their uncertainty and scatter more than at the gas and supercritical states. This scatter resembles the different cutoff radii used in the simulations with different particle numbers, especially for the smallest systems.

Furthermore, the results for the two entropy definitions exhibit a different dependence on the number of particles. At the gas state, the dependence of the results for the temperature on the number of particles for the second definition, $S \overset{\omega}{=} k_\mathrm{B} \ln \omega$, is larger than for the first definition, $S \overset{\Omega}{=} k_\mathrm{B} \ln \Omega$. For the density, the effect is reversed; i.e., the slope of the linear fit for the results obtained with the first definition is much larger than for the results calculated with the second definition. The opposite behavior is observed for the liquid and supercritical states. Nevertheless, in all cases both linear fit functions intercept in the thermodynamic limit and yield the same values for the temperature within much less than their uncertainty. Hence, the results obtained with both definitions for the entropy become numerically equivalent in the thermodynamic limit $N \to \infty$ as predicted by theory.

The relative expanded uncertainty (at the 0.95 confidence level) in temperature is 7 parts per million (ppm) at the gas, 120 ppm at the liquid, and 53 ppm at the supercritical state, while in density it amounts to 8 ppm at the gas, 30 ppm at the liquid, and 37 ppm at the supercritical state. The density at the gas and supercritical states agrees with the EOS within -14 ppm and $+78$ ppm, while the deviation of $+540$ ppm at the liquid state is much larger. At all three states, the agreement is well within the uncertainty of the EOS.

Figure 2 depicts the simulation results for selected further properties, the isochoric and isobaric heat capacities, the isothermal compressibility, and the speed of sound, as a function of the inverse particle number. These properties are related to second-order derivatives of the entropy. The uncertainties of the simulation results are larger than for the temperature and density, and the data scatter more. Again, the extrapolated values for both definitions of the entropy agree with each other well within their uncertainty and become numerically equivalent in the thermodynamic limit. The results for the isochoric heat capacity and speed of sound agree best with the EOS and show deviations below 0.25%.

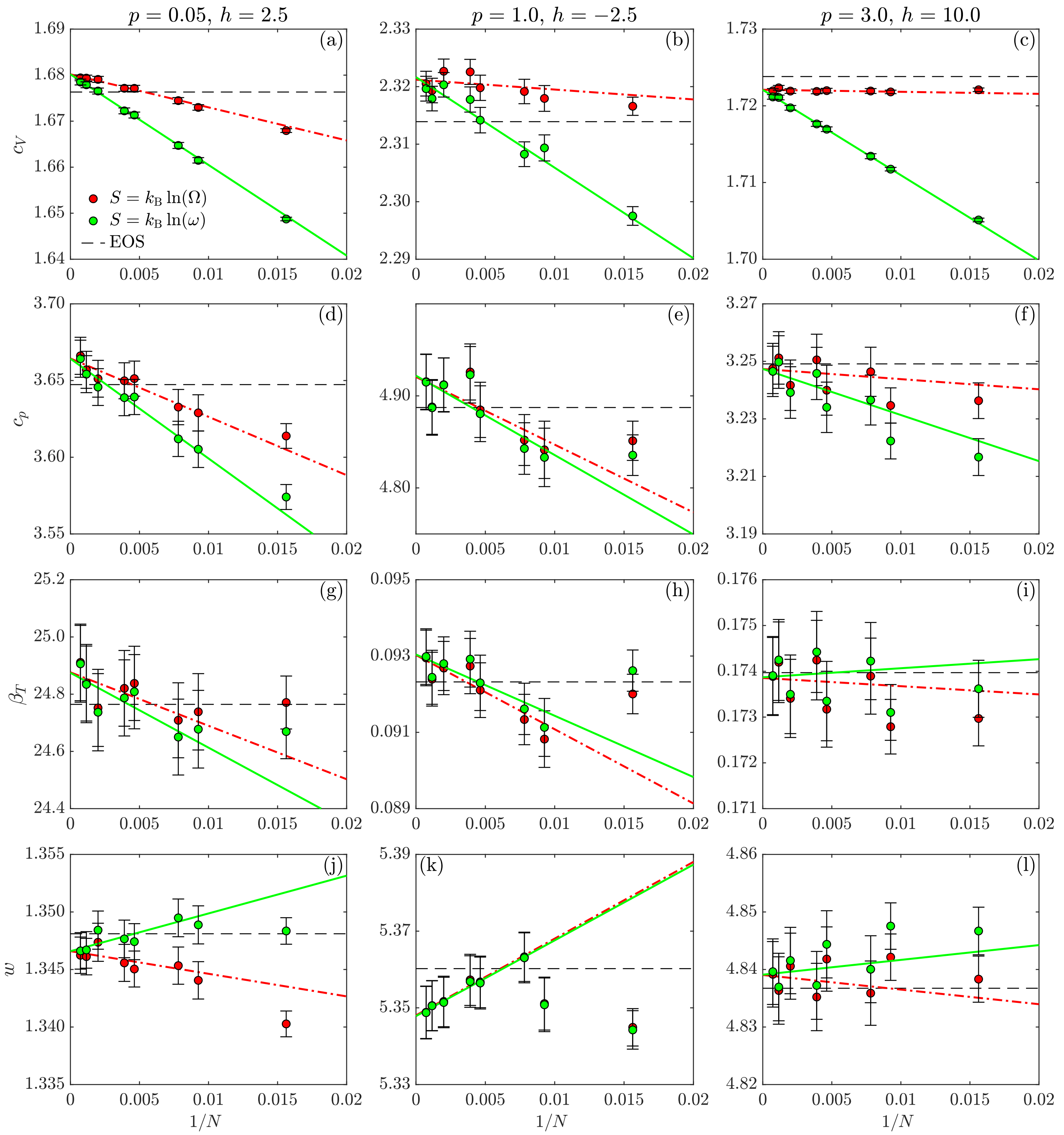

FIG. 2. (a–l) Results of the Monte Carlo simulations for selected thermodynamic properties at three state points of the Lennard-Jones model fluid as a function of the inverse number of particles. The solid green and dash-dotted red lines represent weighted linear least-squares fits to the data, the error bars show the uncertainty in the simulation results, and the dashed black lines represent values calculated with the EOS of Thol *et al.* [37].

For the isobaric heat capacity and isothermal compressibility, the deviations from the EOS are 0.46% and 0.44% at the gas state and 0.7% and 0.8% at the liquid state, respectively. At the supercritical state, these properties agree with the EOS within 0.1%. Among the properties not shown in Fig. 2, the results for thermal pressure coefficients agree best with the EOS, within 0.15%. The largest deviations from the EOS are observed for the Joule-Thomson coefficient with up to +1.5% at the liquid state. In all cases, the agreement is within the uncertainty of the EOS. In summary, the very good agreement between the simulation results and the EOS confirms that the equations derived in Sec. II are correct.

IV. CONCLUSIONS

We applied the methodology developed by Lustig to derive rigorous expressions for all common thermodynamic properties and derivatives of the entropy up to third order in the *NpH* ensemble. In this formalism, derivatives of the thermodynamic potential and thermodynamic properties are represented in a systematic way by phase-space functions. The phase-space functions are ensemble averages of combinations of the kinetic energy and volume of the system. The formalism is elaborated for two definitions of the entropy, with the phase-space volume and with the phase-space density. Both entropy definitions yield different equations for thermodynamic properties in terms of phase-space functions, but values for thermodynamic properties obtained with both definitions become numerically equivalent in the thermodynamic limit. Thus, both definitions are equally useful for calculating macroscopic thermodynamic properties. Moreover, a general expression for phase-space functions was derived, which allows the calculation of derivatives of the entropy of arbitrary order. All derived expressions are applicable to pure fluids consisting of spherical particles, rigid linear molecules, and rigid nonlinear molecules. The generalization to mixtures is also straightforward, but not pursued in this work.

Compared to the canonical and microcanonical ensembles, the expressions for thermodynamic properties in the *NpH* ensemble do not require the calculation of volume derivatives of the intermolecular potential, but contain only ensemble averages of combinations of the kinetic energy and volume of the system. This is advantageous in simulations with empirical force fields or *ab initio* potential energy surfaces for real molecules, which are much more complex than the simple Lennard-Jones potential, because the effort for the calculation of properties related to second or higher-order derivatives of the thermodynamic potential is much smaller than in isochoric ensembles, in which the volume is an independent variable.

Furthermore, the implementation of temperature-dependent potentials that are applied in molecular simulations for real fluids to account for quantum effects semiclassically, e.g., the Feynman-Hibbs quantum corrections [62], is also straightforward in the *NpH* ensemble. Since no derivatives with respect to temperature are formed, the temperature-dependent potential can directly be inserted in the expressions for phase-space functions in Table I. An estimate for the temperature of the simulated state point must be determined beforehand by a short separate simulation, in which the temperature-dependent part of the potential is neglected. Since the contribution of quantum effects to the thermodynamic properties is often small, especially at high temperature, this introduces only a small additional contribution to the uncertainty of the results in most cases.

The derived equations were validated by Monte Carlo simulations of the simple Lennard-Jones model fluid as a test case at three characteristic state points. The simulation results obtained with the formalisms for both entropy definitions converge in the thermodynamic limit. Thus, the expressions for both entropy definitions yield numerically equivalent results and can be applied to calculate properties of macroscopic systems. The results for all properties agree well with a recent equation of state for the Lennard-Jones model fluid, which validates the derived equations.

The formalism developed here can also be applied in molecular-dynamics simulations in the *NpH* ensemble. However, in molecular-dynamics simulations the numbers of degrees of freedom of the particles, $3N$, is reduced by the number of independent constants of motion of the molecular-dynamics algorithm, e.g., the components of the total momentum vector of the system or the components of the vector $\mathbf{G}$, which is related to the initial position of the center of mass of the system. In an exact treatment, this effect must be taken into account in the derivation of the expressions for thermodynamic properties. It results in modified expressions for thermodynamic properties, in which $3N$ is reduced by the number of independent constants of motion. Since the number of constants of motion is small compared to the number of degrees of freedom of the particles, neglecting this effect introduces only small systematic errors in the results for thermodynamic properties if systems with large particle numbers are simulated. If the results of a series of simulations with different particle numbers are extrapolated into the thermodynamic limit, the error vanishes, and results for macroscopic systems are obtained. An extension of the formalism to include the reduction of the numbers of freedom requires a thorough analysis of the equations of motion of the applied molecular-dynamics algorithm and is outside the scope of this work.

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