Classical statistical mechanics in the $\mu V L$ and $\mu p R$ ensembles

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Molecular expressions for thermodynamic properties and derivatives of the entropy up to third order in the adiabatic grand-isochoric $\mu V L$ and adiabatic grand-isobaric $\mu p R$ ensembles are systematically derived 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 by phase-space functions, which represent derivatives of the entropy with respect to the chemical potential, the volume, and the Hill energy L in the $\mu V L$ ensemble and with respect to the chemical potential, the pressure, and the Ray energy R in the $\mu p R$ ensemble. The derived expressions are validated for both ensembles by Monte Carlo simulations for the simple Lennard-Jones model fluid at three selected state points.

I. INTRODUCTION

In statistical mechanics, eight basic ensembles are available, in which thermodynamic properties of pure fluids can be calculated [1]. Each ensemble is characterized by a thermodynamic potential, three independent variables, and a weight factor, which describes the probability distribution of systems in the ensemble. The well-known microcanonical (NVE), canonical (NVT), and grand-canonical (μVT) ensembles were already introduced by Gibbs [2]. In 1939, Guggenheim [3] proposed the isobaric-isothermal (NpT) and generalized (μpT) ensembles. The canonical, grand-canonical, isothermal-isobaric, and generalized ensembles are isothermal ensembles, in which the temperature T of the system is held constant by exchanging heat with a constant temperature reservoir. However, the microcanonical ensemble represents adiabatic systems at constant energy E, which cannot exchange heat with their environment. A further adiabatic ensemble, the isoenthalpic-isobaric (NpH) ensemble, in which the number of particles N, the pressure p, and the enthalpy H are independent variables, was suggested by Byers Brown [4] in 1958. After Andersen had proposed an algorithm for molecular-dynamics simulations in the isoenthalpic-isobaric ensemble [5], Haile and Graben [6], Ray *et al.* [7], and Ray and Graben [8] developed the theory of this second adiabatic ensemble.

In 1981, Ray *et al.* [9] introduced a third adiabatic ensemble, the $\mu V L$ ensemble, in which the chemical potential μ, the volume V, and the quantity L are the independent variables. The quantity L is defined by $L = E - \mu N$ and termed Hill energy because it was originally introduced by Hill [10]. Since the chemical potential is prescribed and the number of particles fluctuates, it represents open systems. Ray *et al.*

regarded the $\mu V L$ ensemble as the adiabatic counterpart of the isothermal grand-canonical ensemble.

A fourth adiabatic ensemble for simulating open systems at constant pressure, the $\mu p R$ ensemble, was proposed by Ray and Graben in 1990 [11]. Here, the chemical potential, the pressure, and the quantity R are the independent variables. The prescribed quantity $R = E - \mu N + pV$ is the Ray energy. This adiabatic ensemble corresponds to the isothermal generalized ensemble. Ray and Wolf extended the Metropolis algorithm for Monte Carlo simulations in the $\mu p R$ ensemble [12] and pointed out that the $\mu p R$ ensemble is the only meaningful ensemble for carrying out simulations of open systems at constant pressure since in the generalized ensemble only intensive variables are prescribed and the system size is not specified [13]. Ray and Graben also provided equations for the calculation of the isobaric heat capacity, thermal expansion coefficient, and isentropic compressibility at constant chemical potential in the $\mu p R$ ensemble [11].

A common description of the four adiabatic ensembles and their interrelations was provided by Graben and Ray [14]. In a similar manner, Graben and Ray presented a unified treatment of all eight basic ensembles of statistical mechanics and their interrelations by a Laplace-Legendre tranformation scheme [1]. In all four adiabatic ensembles, the entropy S is the thermodynamic potential as a function of the independent variables of the ensemble, i.e., $S = S(N, V, E)$, $S = S(N, p, H)$, $S = S(\mu, V, L)$, and $S = S(\mu, p, R)$. Thermodynamic properties are obtained as combinations of derivatives of the entropy with respect to the independent variables.

Some applications of the $\mu V L$ and $\mu p R$ ensembles are described in the literature. Çagin and Pettitt developed a method for molecular-dynamics simulations in the $\mu V L$ ensemble [15,16] and grand-canonical ensemble [16], which is based on an extended Lagrangian that accounts for coupling of the simulated system to a chemical potential reservoir and allows for dynamical particle insertions and deletions. They provided

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expressions for the calculation of the isochoric heat capacity, the Grüneisen parameter and isentropic compressibility at constant chemical potential in the μVL ensemble [16]. This method was subsequently refined by Pettitt and coworkers [17,18] for the grand-canonical ensemble.

Kristóf and Liszi [19,20] proposed Gibbs ensembles at constant μVL and μpR for the simulation of the vapor-liquid equilibria of pure fluids and mixtures. Escobedo [21] developed a unified framework with which advanced Monte Carlo methods such as multihistogram reweighting and replica-exchange methods can be applied to different adiabatic ensembles including the μVL and μpR ensembles.

Desgranges and Delhommelle examined several applications of the μpR ensemble [22] in Monte Carlo simulations. They pointed out that the entropy can be directly calculated by the relation $S = R/T$, since the temperature can readily be computed by the equipartition theorem. Moreover, they showed how the vapor-liquid coexistence curve of pure fluids can be mapped by Monte Carlo simulations along isobars in the temperature–entropy diagram by using model potentials for argon and copper as examples. They also described the calculation of enthalpy changes in isentropic processes in the μpR ensemble, which are often encountered in engineering applications. In a subsequent work, Desgranges and Delhommelle [23] extended the μpR ensemble to mixtures and applied it to calculate the enthalpy, entropy, and Gibbs energy of mixing of binary mixtures of the noble gases argon and neon by Monte Carlo simulations.

Lustig devised a methodology for the systematic derivation of expressions for thermodynamic properties in the molecular-dynamics ensemble [24–28], in which in addition to the number of particles, the volume, and the energy, the total momentum $\mathbf{P}$ and a quantity $\mathbf{G}$, which is related to the center of mass, are constants of motion. It enables the derivation of expressions for thermodynamic properties without any approximations in contrast to fluctuation theory, with which only approximate expressions can be derived. Key to this methodology is the introduction of phase-space functions to systematically represent derivatives of the phase-space volume of the respective ensemble. Lustig subsequently applied this methodology to derive expressions for thermodynamic properties in the microcanonical [28] and canonical [29,30] ensembles. Recently, we applied the Lustig methodology to derive expressions for thermodynamic properties and derivatives of the thermodynamic potential up to the third order in the isothermal-isobaric ensemble [31], the grand-canonical ensemble [32], and the isoenthalpic-isobaric ensemble [33]. In this article, we continue these works and apply the Lustig methodology to derive rigorous expressions for thermodynamic properties and derivatives of the entropy S up to third order in the μVL and μpR ensembles.

This article is organized as follows. Sections II and III establish the theoretical background for the calculation of thermodynamic properties and provide the expressions for the most important thermodynamic properties and derivatives of the entropy up to third order in the μVL and μpR ensembles. The derived equations are validated by Monte Carlo simulations at three state points with the simple Lennard-Jones model fluid in Sec. IV, and Sec. V presents conclusions.

II. EXPRESSIONS FOR THERMODYNAMIC PROPERTIES IN THE μVL ENSEMBLE

In the μVL ensemble, the entropy S is the thermodynamic potential, and the chemical potential μ, the volume V, and the Hill energy $L = E - \mu N$ are the independent variables. In analogy to the adiabatic NVE and NpH ensembles, the phase-space volume of the μVL ensemble

$$\Omega(\mu, V, L) = \sum_{N=0}^{\infty} \frac{1}{N! h^{3N}} \iint \Theta(L + \mu N - \mathscr{H}) d\mathbf{r}^N d\mathbf{p}^N \tag{1}$$

is introduced, where Θ is the Heaviside step function, h is the Planck constant, and $d\mathbf{r}^N$ and $d\mathbf{p}^N$ represent integrations over the $3N$ coordinates and $3N$ momenta of the particles. The symbol $\mathscr{H}$ denotes the Hamiltonian of the microcanonical ensemble. The phase-space density of the μVL ensemble is the derivative of the phase-space volume with respect to the Hill energy $\omega = d\Omega/dL$. It is defined by

$$\omega(\mu, V, L) = \sum_{N=0}^{\infty} \frac{1}{N! h^{3N}} \iint \delta(L + \mu N - \mathscr{H}) d\mathbf{r}^N d\mathbf{p}^N, \tag{2}$$

in which δ denotes the Dirac δ function. As in all adiabatic ensembles, the entropy can either be defined with the phase-space volume by

$$S(\mu, V, L) = k_B \ln \Omega(\mu, V, L) \tag{3}$$

or with the phase-space density by

$$S(\mu, V, L) = k_B \ln \omega(\mu, V, L), \tag{4}$$

where k_B denotes the Boltzmann constant. Both definitions will yield different expressions for thermodynamic properties. In the literature, some authors prefer the definition with the phase-space volume [34–36], while others use the definition with the phase-space density [25,37,38]. Attempts to provide evidence for discriminating between both definitions have so far not been conclusive [27,28,39]. Becker argued that both definitions become equivalent in the thermodynamic limit [40]. Lustig [27,28] and Ströker and Meier [33] observed that numerical results for thermodynamic properties in the thermodynamic limit obtained from Monte Carlo simulations in the microcanonical and isoenthalpic-isobaric ensembles with expressions based on both definitions agree within their statistical uncertainty. Since this behavior can also be expected in the μVL ensemble, we derive expressions for thermodynamic properties for both entropy definitions in the following. The equivalence of both definitions in the thermodynamic limit will be discussed in Sec. IV with Monte Carlo simulation results for the Lennard-Jones model fluid.

The derivation of expressions for thermodynamic properties proceeds in two steps. First, derivatives of the entropy with respect to the independent variables and equations for thermodynamic properties are expressed by phase-space functions. In the second step, equations for the phase-space functions in terms of ensemble averages of combinations of powers of instantaneous values of the kinetic energy, volume derivatives of the potential, and number of particles are derived. This is achieved by comparing derivatives of the phase space volume with a general equation for an ensemble average of an arbitrary quantity in the μVL ensemble.

In the first step, derivatives of the entropy with respect to the Hill energy, volume and chemical potential are expressed in a systematic way by derivatives of the phase-space volume Ω or phase-space density ω with respect to L, V, and μ. Derivatives of the entropy are abbreviated by

$$\mathcal{S}_{mno} \overset{\Omega}{=} \frac{\partial^{m+n+o} \ln \Omega}{\partial L^m \partial V^n \partial \mu^o}, \quad m, n, o = 0, 1, 2, \dots \quad (5)$$

and

$$\mathcal{S}_{mno} \overset{\omega}{=} \frac{\partial^{m+n+o} \ln \omega}{\partial L^m \partial V^n \partial \mu^o}, \quad m, n, o = 0, 1, 2, \dots, \quad (6)$$

where the notations $\overset{\Omega}{=}$ and $\overset{\omega}{=}$ refer to the entropy definitions with the phase-space volume and phase-space density, respectively. The phase-space functions of the μVL ensemble are defined by

$$\Omega_{mno} = \frac{1}{\omega} \frac{\partial^{m+n+o} \Omega}{\partial L^m \partial V^n \partial \mu^o}, \quad m, n, o = 0, 1, 2, \dots. \quad (7)$$

Note the special case

$$\Omega_{100} = \frac{1}{\omega} \frac{\partial \Omega}{\partial L} = 1. \quad (8)$$

By applying the product rule on Eq. (7), the three recurrence relations

$$\frac{\partial \Omega_{mno}}{\partial L} = \Omega_{m+1,n,o} - \Omega_{200} \Omega_{mno}, \quad m + n + o \geqslant 1, \quad (9)$$

$$\frac{\partial \Omega_{mno}}{\partial V} = \Omega_{m,n+1,o} - \Omega_{110} \Omega_{mno}, \quad m + n + o \geqslant 1, \quad (10)$$

$$\frac{\partial \Omega_{mno}}{\partial \mu} = \Omega_{m,n,o+1} - \Omega_{101} \Omega_{mno}, \quad m + n + o \geqslant 1, \quad (11)$$

can be established. They are useful for calculating higher-order derivatives of phase-space functions with respect to L, V, and μ.

In the formalism for the entropy definition with the phase-space volume, the first derivative of the entropy with respect to the Hill energy yields

$$\mathcal{S}_{100} \overset{\Omega}{=} \frac{\partial \ln \Omega}{\partial L} = \frac{1}{\Omega} \frac{\partial \Omega}{\partial L} = \frac{\omega}{\Omega} = \Omega_{000}^{-1}, \quad (12)$$

where $\omega = \partial \Omega / \partial L$ and Eq. (7) have been used. Similarly, the derivatives with respect to volume and chemical potential are obtained as

$$\mathcal{S}_{010} \overset{\Omega}{=} \frac{\partial \ln \Omega}{\partial V} = \frac{1}{\Omega} \frac{\partial \Omega}{\partial V} = \frac{1}{\Omega} \frac{\omega}{\omega} \frac{\partial \Omega}{\partial V} = \Omega_{000}^{-1} \Omega_{010} \quad (13)$$

and

$$\mathcal{S}_{001} \overset{\Omega}{=} \frac{\partial \ln \Omega}{\partial \mu} = \frac{1}{\Omega} \frac{\partial \Omega}{\partial \mu} = \frac{1}{\Omega} \frac{\omega}{\omega} \frac{\partial \Omega}{\partial \mu} = \Omega_{000}^{-1} \Omega_{001}. \quad (14)$$

If the definition of the entropy with the phase-space density is used, the first partial derivatives are given by

$$\mathcal{S}_{100} \overset{\omega}{=} \frac{\partial \ln \omega}{\partial L} = \frac{1}{\omega} \frac{\partial \omega}{\partial L} = \frac{1}{\omega} \frac{\partial^2 \Omega}{\partial L^2} = \Omega_{200}, \quad (15)$$

$$\mathcal{S}_{010} \overset{\omega}{=} \frac{\partial \ln \omega}{\partial V} = \frac{1}{\omega} \frac{\partial \omega}{\partial V} = \frac{1}{\omega} \frac{\partial^2 \Omega}{\partial V \partial L} = \Omega_{110}, \quad (16)$$

$$\mathcal{S}_{001} \overset{\omega}{=} \frac{\partial \ln \omega}{\partial \mu} = \frac{1}{\omega} \frac{\partial \omega}{\partial \mu} = \frac{1}{\omega} \frac{\partial^2 \Omega}{\partial \mu \partial L} = \Omega_{101}. \quad (17)$$

Starting with the first-order derivatives, the recurrence relations can be used to readily calculate derivatives of higher orders. Derivatives up to third order for both entropy definitions are listed in Table I. The expressions in the right column of Table I simplify because $\Omega_{100} = 1$. The expressions for the derivatives of the entropy with respect to the Hill energy and the volume have the same mathematical structure as the corresponding relations for derivatives of the entropy in the microcanonical ensemble with respect to the energy and the volume [30]. However, in the μVL ensemble additionally derivatives with respect to the third independent variable, the chemical potential μ, must be formed because they are required when transforming partial derivatives at constant chemical potential into derivatives at constant number of particles.

The expressions for the derivatives of the entropy S_{mno} and all thermodynamic properties for both entropy definitions are interrelated because the same definition of phase-space functions is used in the expressions derived with both entropy definitions and the phase-space density is the derivative of the phase-space volume. For this reason, they can be transformed into each other. The transformation of expressions for the entropy definition with the phase-space volume into those for the entropy definition with the space-space density is performed by replacing each phase-space function Ω_{mno} by $\Omega_{m+1,n,o} \Omega_{200}^{-1}$. Similarly, the inverse transformation of an expression for the entropy definition with ω into one for Ω is carried out by replacing each phase-space function Ω_{mno} by $\Omega_{m-1,n,o} \Omega_{000}^{-1}$. These transformation rules are similar to those described by Lustig [25,28] for the microcanonical ensemble and by Ströker et al. [33] for the NpH ensemble. A proof of the transformation rules was already given in our previous work on the NpH ensemble [33] and is therefore omitted here. In the following, expressions for thermodynamic properties are only derived in detail for the entropy definition with the phase-space volume since the expressions for the entropy definition with the phase-space density can readily be obtained by applying the transformation rule.

First, expressions for the temperature, the pressure, and the number of particles in terms of the phase-space functions are derived. These three quantities are related to first-order derivatives of the entropy and are required for the derivation of expressions for other thermodynamic properties. The total differential of the thermodynamic potential $S = S(\mu, V, L)$ is given by [1]

$$dS = \frac{1}{T} dL + \frac{p}{T} dV + \frac{N}{T} d\mu. \quad (18)$$

The inverse temperature is the derivative of entropy with respect to the Hill energy at constant chemical potential and volume and can be related to the phase space function Ω_{000} by

$$\frac{1}{T} = \left(\frac{\partial S}{\partial L} \right)_{V,\mu} = k_{\mathrm{B}} \mathcal{S}_{100} \overset{\Omega}{=} k_{\mathrm{B}} \Omega_{000}^{-1}. \quad (19)$$

Thus, the expression for the temperature follows as

$$T \overset{\Omega}{=} k_{\mathrm{B}}^{-1} \Omega_{000}. \quad (20)$$

Using Eq. (20) and the expression for $\mathcal{S}_{010}$ from Table I, the expression for the pressure reads

$$p = T \left(\frac{\partial S}{\partial V} \right)_{L,\mu} = T k_{\mathrm{B}} \mathcal{S}_{010} \overset{\Omega}{=} \Omega_{010}. \quad (21)$$

TABLE I. Expressions for partial derivatives $\mathcal{S}_{mno}$ of $\ln \Omega(\mu, V, L)$ and $\ln \omega(\mu, V, L)$ up to third order in terms of phase-space functions Ω_{mno}. The expressions for partial derivatives $\mathcal{S}_{mno}$ of $\ln \Omega(\mu, p, R)$ and $\ln \omega(\mu, p, R)$ in the μpR ensemble are identical with the first index m referring to the Ray energy R and the second index n to the pressure p.

$S \stackrel{\Omega}{=} k_B \ln \Omega$	$S \stackrel{\omega}{=} k_B \ln \omega$
$\mathcal{S}_{100} \stackrel{\Omega}{=} \Omega_{000}^{-1}$	$\mathcal{S}_{100} \stackrel{\omega}{=} \Omega_{200}$
$\mathcal{S}_{200} \stackrel{\Omega}{=} -\Omega_{000}^{-2} + \Omega_{000}^{-1}\Omega_{200}$	$\mathcal{S}_{200} \stackrel{\omega}{=} -\Omega_{200}^2 + \Omega_{300}$
$\mathcal{S}_{300} \stackrel{\Omega}{=} 2\Omega_{000}^{-3} - 3\Omega_{000}^{-2}\Omega_{200} + \Omega_{000}^{-1}\Omega_{300}$	$\mathcal{S}_{300} \stackrel{\omega}{=} 2\Omega_{200}^3 - 3\Omega_{200}\Omega_{300} + \Omega_{400}$
$\mathcal{S}_{010} \stackrel{\Omega}{=} \Omega_{000}^{-1}\Omega_{010}$	$\mathcal{S}_{010} \stackrel{\omega}{=} \Omega_{110}$
$\mathcal{S}_{020} \stackrel{\Omega}{=} -\Omega_{000}^{-2}\Omega_{010}^2 + \Omega_{000}^{-1}\Omega_{020}$	$\mathcal{S}_{020} \stackrel{\omega}{=} -\Omega_{110}^2 + \Omega_{120}$
$\mathcal{S}_{030} \stackrel{\Omega}{=} 2\Omega_{000}^{-3}\Omega_{010}^3 - 3\Omega_{000}^{-2}\Omega_{020}\Omega_{010} + \Omega_{000}^{-1}\Omega_{030}$	$\mathcal{S}_{030} \stackrel{\omega}{=} 2\Omega_{110}^3 - 3\Omega_{120}\Omega_{110} + \Omega_{130}$
$\mathcal{S}_{001} \stackrel{\Omega}{=} \Omega_{000}^{-1}\Omega_{001}$	$\mathcal{S}_{001} \stackrel{\omega}{=} \Omega_{101}$
$\mathcal{S}_{002} \stackrel{\Omega}{=} -\Omega_{000}^{-2}\Omega_{001}^2 + \Omega_{000}^{-1}\Omega_{002}$	$\mathcal{S}_{002} \stackrel{\omega}{=} -\Omega_{101}^2 + \Omega_{102}$
$\mathcal{S}_{003} \stackrel{\Omega}{=} 2\Omega_{000}^{-3}\Omega_{001}^3 - 3\Omega_{000}^{-2}\Omega_{002}\Omega_{001} + \Omega_{000}^{-1}\Omega_{003}$	$\mathcal{S}_{003} \stackrel{\omega}{=} 2\Omega_{101}^3 - 3\Omega_{102}\Omega_{101} + \Omega_{103}$
$\mathcal{S}_{110} \stackrel{\Omega}{=} -\Omega_{000}^{-2}\Omega_{010} + \Omega_{000}^{-1}\Omega_{110}$	$\mathcal{S}_{110} \stackrel{\omega}{=} -\Omega_{200}\Omega_{110} + \Omega_{210}$
$\mathcal{S}_{101} \stackrel{\Omega}{=} -\Omega_{000}^{-2}\Omega_{001} + \Omega_{000}^{-1}\Omega_{101}$	$\mathcal{S}_{101} \stackrel{\omega}{=} -\Omega_{200}\Omega_{101} + \Omega_{201}$
$\mathcal{S}_{011} \stackrel{\Omega}{=} -\Omega_{000}^{-2}\Omega_{010}\Omega_{001} + \Omega_{000}^{-1}\Omega_{011}$	$\mathcal{S}_{011} \stackrel{\omega}{=} -\Omega_{110}\Omega_{101} + \Omega_{111}$
$\mathcal{S}_{120} \stackrel{\Omega}{=} 2\Omega_{000}^{-3}\Omega_{010}^2 - 2\Omega_{000}^{-2}\Omega_{110}\Omega_{010} - \Omega_{000}^{-2}\Omega_{020} + \Omega_{000}^{-1}\Omega_{120}$	$\mathcal{S}_{120} \stackrel{\omega}{=} 2\Omega_{200}\Omega_{110}^2 - 2\Omega_{210}\Omega_{110} - \Omega_{200}\Omega_{120} + \Omega_{220}$
$\mathcal{S}_{210} \stackrel{\Omega}{=} 2\Omega_{000}^{-3}\Omega_{010} - \Omega_{000}^{-2}\Omega_{200}\Omega_{010} - 2\Omega_{000}^{-2}\Omega_{110} + \Omega_{000}^{-1}\Omega_{210}$	$\mathcal{S}_{210} \stackrel{\omega}{=} 2\Omega_{200}^2\Omega_{110} - \Omega_{300}\Omega_{110} - 2\Omega_{200}\Omega_{210} + \Omega_{310}$
$\mathcal{S}_{102} \stackrel{\Omega}{=} 2\Omega_{000}^{-3}\Omega_{001}^2 - 2\Omega_{000}^{-2}\Omega_{101}\Omega_{001} - \Omega_{000}^{-2}\Omega_{002} + \Omega_{000}^{-1}\Omega_{102}$	$\mathcal{S}_{102} \stackrel{\omega}{=} 2\Omega_{200}\Omega_{101}^2 - 2\Omega_{201}\Omega_{101} - \Omega_{200}\Omega_{102} + \Omega_{202}$
$\mathcal{S}_{201} \stackrel{\Omega}{=} 2\Omega_{000}^{-3}\Omega_{001} - \Omega_{000}^{-2}\Omega_{200}\Omega_{001} - 2\Omega_{000}^{-2}\Omega_{101} + \Omega_{000}^{-1}\Omega_{201}$	$\mathcal{S}_{201} \stackrel{\omega}{=} 2\Omega_{200}^2\Omega_{101} - \Omega_{300}\Omega_{101} - 2\Omega_{200}\Omega_{201} + \Omega_{301}$
$\mathcal{S}_{012} \stackrel{\Omega}{=} 2\Omega_{000}^{-3}\Omega_{001}^2\Omega_{010} - \Omega_{000}^{-2}(2\Omega_{011}\Omega_{001} + \Omega_{002}\Omega_{010}) + \Omega_{000}^{-1}\Omega_{012}$	$\mathcal{S}_{012} \stackrel{\omega}{=} 2\Omega_{101}(\Omega_{101}\Omega_{110} - \Omega_{111}) - \Omega_{102}\Omega_{110} + \Omega_{112}$
$\mathcal{S}_{021} \stackrel{\Omega}{=} 2\Omega_{000}^{-3}\Omega_{010}^2\Omega_{001} - \Omega_{000}^{-2}(2\Omega_{011}\Omega_{010} + \Omega_{020}\Omega_{001}) + \Omega_{000}^{-1}\Omega_{021}$	$\mathcal{S}_{021} \stackrel{\omega}{=} 2\Omega_{110}(\Omega_{110}\Omega_{101} - \Omega_{111}) - \Omega_{120}\Omega_{101} + \Omega_{121}$
$\mathcal{S}_{111} \stackrel{\Omega}{=} 2\Omega_{000}^{-3}\Omega_{010}\Omega_{001} - \Omega_{000}^{-2}(\Omega_{110}\Omega_{001} + \Omega_{010}\Omega_{101} + \Omega_{011}) + \Omega_{000}^{-1}\Omega_{111}$	$\mathcal{S}_{111} \stackrel{\omega}{=} \Omega_{200}(2\Omega_{101}\Omega_{110} - \Omega_{111}) - \Omega_{210}\Omega_{101} - \Omega_{110}\Omega_{201} + \Omega_{211}$

Similarly, the expression for the number of particles

$$N = T\left(\frac{\partial S}{\partial \mu}\right)_{L,V} = Tk_B\mathcal{S}_{001} \stackrel{\Omega}{=} \Omega_{001} \tag{22}$$

is found. By applying the recurrence relations, Eqs. (9) to (11), to Eqs. (20) to (22), expressions for the derivatives of the temperature, pressure, and number of particles with respect to L, V, and μ in terms of phase-space functions can be obtained. These expressions are summarized for both entropy definitions in Table II.

With the equations in Table II, expressions for further thermodynamic properties can be established. Since all major

thermodynamic properties are defined at a constant number of particles, but in the μVL ensemble the chemical potential is an independent variable, partial derivatives at constant chemical potential must be transformed into derivatives at constant number of particles. This transformation is performed by the method of Jacobian determinants described by Münster [41], which was also used by Lustig [30] and us [31–33] in the derivation of expressions for thermodynamic properties in other ensembles. As the volume is an independent variable in the μVL ensemble, expressions for isochoric properties can readily be obtained. The defining equation for the isochoric heat capacity can be transformed into

$$C_V = \left(\frac{\partial E}{\partial T}\right)_{V,N} = \frac{\partial(E,N)}{\partial(T,N)} = \frac{\frac{\partial(E,N)}{\partial(L,\mu)}}{\frac{\partial(T,N)}{\partial(L,\mu)}} = \frac{\begin{vmatrix} \left(\frac{\partial E}{\partial L}\right)_{V,\mu} & \left(\frac{\partial E}{\partial \mu}\right)_{L,V} \\ \left(\frac{\partial N}{\partial L}\right)_{V,\mu} & \left(\frac{\partial N}{\partial \mu}\right)_{L,V} \end{vmatrix}}{\begin{vmatrix} \left(\frac{\partial T}{\partial L}\right)_{V,\mu} & \left(\frac{\partial T}{\partial \mu}\right)_{L,V} \\ \left(\frac{\partial N}{\partial L}\right)_{V,\mu} & \left(\frac{\partial N}{\partial \mu}\right)_{L,V} \end{vmatrix}} = \frac{\left(\frac{\partial N}{\partial \mu}\right)_{L,V} - N\left(\frac{\partial N}{\partial L}\right)_{V,\mu}}{\left(\frac{\partial T}{\partial L}\right)_{V,\mu}\left(\frac{\partial N}{\partial \mu}\right)_{L,V} - \left(\frac{\partial N}{\partial L}\right)_{V,\mu}\left(\frac{\partial T}{\partial \mu}\right)_{L,V}}, \tag{23}$$

in which E denotes the internal energy. When the number of particles and the partial derivatives are replaced by the expressions in Table II, an equation for the isochoric heat capacity in terms of phase-space functions is found. This step is omitted here since it results in a lengthy equation for C_V. If the isochoric heat capacity is calculated in a simulation, a stepwise procedure should be applied. First, the number of particles and all partial derivatives are calculated by the equations in Table II, and the numerical

TABLE II. Expressions for the temperature T, the pressure p, and the number of particles N and their partial derivatives with respect to Hill energy L, volume V, and chemical potential μ in terms of phase-space functions Ω_{mno} for both entropy definitions in the μVL ensemble. The corresponding expressions for the μpR ensemble are obtained by exchanging V with p and L with R.

$$T = \left[\left(\frac{\partial S}{\partial L} \right)_{V,\mu} \right]^{-1} \overset{\Omega}{=} k_{\mathrm{B}}^{-1} \Omega_{000} \qquad p = T \left(\frac{\partial S}{\partial V} \right)_{L,\mu} \overset{\Omega}{=} \Omega_{010} \qquad N = T \left(\frac{\partial S}{\partial \mu} \right)_{L,V} \overset{\Omega}{=} \Omega_{001}$$

$$\left(\frac{\partial T}{\partial L} \right)_{V,\mu} \overset{\Omega}{=} k_{\mathrm{B}}^{-1}(1 - \Omega_{000}\Omega_{200}) \qquad \left(\frac{\partial p}{\partial L} \right)_{V,\mu} \overset{\Omega}{=} \Omega_{110} - \Omega_{010}\Omega_{200} \qquad \left(\frac{\partial N}{\partial L} \right)_{V,\mu} \overset{\Omega}{=} \Omega_{101} - \Omega_{001}\Omega_{200}$$

$$\left(\frac{\partial T}{\partial V} \right)_{L,\mu} \overset{\Omega}{=} k_{\mathrm{B}}^{-1}(\Omega_{010} - \Omega_{000}\Omega_{110}) \qquad \left(\frac{\partial p}{\partial V} \right)_{L,\mu} \overset{\Omega}{=} \Omega_{020} - \Omega_{010}\Omega_{110} \qquad \left(\frac{\partial N}{\partial V} \right)_{L,\mu} \overset{\Omega}{=} \Omega_{011} - \Omega_{001}\Omega_{110}$$

$$\left(\frac{\partial T}{\partial \mu} \right)_{L,V} \overset{\Omega}{=} k_{\mathrm{B}}^{-1}(\Omega_{001} - \Omega_{000}\Omega_{101}) \qquad \left(\frac{\partial p}{\partial \mu} \right)_{L,V} \overset{\Omega}{=} \Omega_{011} - \Omega_{010}\Omega_{101} \qquad \left(\frac{\partial N}{\partial \mu} \right)_{L,V} \overset{\Omega}{=} \Omega_{002} - \Omega_{001}\Omega_{101}$$

$$T = \left[\left(\frac{\partial S}{\partial L} \right)_{V,\mu} \right]^{-1} \overset{\omega}{=} k_{\mathrm{B}}^{-1} \frac{1}{\Omega_{200}} \qquad p = T \left(\frac{\partial S}{\partial V} \right)_{L,\mu} \overset{\omega}{=} \frac{\Omega_{110}}{\Omega_{200}} \qquad N = T \left(\frac{\partial S}{\partial \mu} \right)_{L,V} \overset{\omega}{=} \frac{\Omega_{101}}{\Omega_{200}}$$

$$\left(\frac{\partial T}{\partial L} \right)_{V,\mu} \overset{\omega}{=} k_{\mathrm{B}}^{-1} \left(1 - \frac{\Omega_{300}}{\Omega_{200}^2} \right) \qquad \left(\frac{\partial p}{\partial L} \right)_{V,\mu} \overset{\omega}{=} \frac{\Omega_{210}}{\Omega_{200}} - \frac{\Omega_{110}\Omega_{300}}{\Omega_{200}^2} \qquad \left(\frac{\partial N}{\partial L} \right)_{V,\mu} \overset{\omega}{=} \frac{\Omega_{201}}{\Omega_{200}} - \frac{\Omega_{101}\Omega_{300}}{\Omega_{200}^2}$$

$$\left(\frac{\partial T}{\partial V} \right)_{L,\mu} \overset{\omega}{=} k_{\mathrm{B}}^{-1} \left(\frac{\Omega_{110}}{\Omega_{200}} - \frac{\Omega_{210}}{\Omega_{200}^2} \right) \qquad \left(\frac{\partial p}{\partial V} \right)_{L,\mu} \overset{\omega}{=} \frac{\Omega_{120}}{\Omega_{200}} - \frac{\Omega_{110}\Omega_{210}}{\Omega_{200}^2} \qquad \left(\frac{\partial N}{\partial V} \right)_{L,\mu} \overset{\omega}{=} \frac{\Omega_{111}}{\Omega_{200}} - \frac{\Omega_{101}\Omega_{210}}{\Omega_{200}^2}$$

$$\left(\frac{\partial T}{\partial \mu} \right)_{L,V} \overset{\omega}{=} k_{\mathrm{B}}^{-1} \left(\frac{\Omega_{101}}{\Omega_{200}} - \frac{\Omega_{201}}{\Omega_{200}^2} \right) \qquad \left(\frac{\partial p}{\partial \mu} \right)_{L,V} \overset{\omega}{=} \frac{\Omega_{111}}{\Omega_{200}} - \frac{\Omega_{110}\Omega_{201}}{\Omega_{200}^2} \qquad \left(\frac{\partial N}{\partial \mu} \right)_{L,V} \overset{\omega}{=} \frac{\Omega_{102}}{\Omega_{200}} - \frac{\Omega_{101}\Omega_{201}}{\Omega_{200}^2}$$

results are inserted into Eq. (23) to obtain the value for C_V. This procedure should also be applied to calculate all other properties that are related to second-order derivatives in the remainder of this section and Sec. III.

By an analogous transformation, an expression for the thermal pressure coefficient is obtained as

$$\gamma_V = \left(\frac{\partial p}{\partial T} \right)_{V,N} = \frac{\partial(p,N)}{\partial(T,N)} = \frac{\frac{\partial(p,N)}{\partial(L,\mu)}}{\frac{\partial(T,N)}{\partial(L,\mu)}} = \frac{\begin{vmatrix} \left(\frac{\partial p}{\partial L} \right)_{V,\mu} & \left(\frac{\partial p}{\partial \mu} \right)_{L,V} \\ \left(\frac{\partial N}{\partial L} \right)_{V,\mu} & \left(\frac{\partial N}{\partial \mu} \right)_{L,V} \end{vmatrix}}{\begin{vmatrix} \left(\frac{\partial T}{\partial L} \right)_{V,\mu} & \left(\frac{\partial T}{\partial \mu} \right)_{L,V} \\ \left(\frac{\partial N}{\partial L} \right)_{V,\mu} & \left(\frac{\partial N}{\partial \mu} \right)_{L,V} \end{vmatrix}} = \frac{\left(\frac{\partial p}{\partial L} \right)_{V,\mu} \left(\frac{\partial N}{\partial \mu} \right)_{L,V} - \left(\frac{\partial N}{\partial L} \right)_{V,\mu} \left(\frac{\partial p}{\partial \mu} \right)_{L,V}}{\left(\frac{\partial T}{\partial L} \right)_{V,\mu} \left(\frac{\partial N}{\partial \mu} \right)_{L,V} - \left(\frac{\partial N}{\partial L} \right)_{V,\mu} \left(\frac{\partial T}{\partial \mu} \right)_{L,V}}. \tag{24}$$

The derivation of an expression for the isothermal compressibility $\beta_T = -V^{-1}(\partial V/\partial p)_{T,N}$ is more complex since the method of Jacobian determinants must be applied twice to transform the derivative at constant temperature into derivatives at constant Hill energy and in the second step derivatives at constant number of particles into derivatives at constant chemical potential. The result for the inverse isothermal compressibility after the twofold transformation reads

$$\beta_T^{-1} = -V \left[\left(\frac{\partial p}{\partial V} \right)_{L,\mu} + \left(\frac{\partial p}{\partial L} \right)_{V,\mu} \frac{\left(\frac{\partial T}{\partial V} \right)_{L,\mu} \left(\frac{\partial N}{\partial \mu} \right)_{L,V} - \left(\frac{\partial T}{\partial \mu} \right)_{L,V} \left(\frac{\partial N}{\partial V} \right)_{L,\mu}}{\left(\frac{\partial N}{\partial L} \right)_{V,\mu} \left(\frac{\partial T}{\partial \mu} \right)_{L,V} - \left(\frac{\partial T}{\partial L} \right)_{V,\mu} \left(\frac{\partial N}{\partial \mu} \right)_{L,V}} + \left(\frac{\partial p}{\partial \mu} \right)_{L,V} \frac{\left(\frac{\partial T}{\partial L} \right)_{V,\mu} \left(\frac{\partial N}{\partial V} \right)_{L,\mu} - \left(\frac{\partial T}{\partial V} \right)_{L,\mu} \left(\frac{\partial N}{\partial L} \right)_{V,\mu}}{\left(\frac{\partial N}{\partial L} \right)_{V,\mu} \left(\frac{\partial T}{\partial \mu} \right)_{L,V} - \left(\frac{\partial T}{\partial L} \right)_{V,\mu} \left(\frac{\partial N}{\partial \mu} \right)_{L,\mu}} \right]. \tag{25}$$

Further properties, e.g., the isobaric thermal expansivity α_p, isobaric heat capacity C_p, isentropic compressibility β_s, speed of sound w, and Joule–Thomson coefficient μ_{JT}, which are related to second-order derivatives of the entropy, can be calculated by these three quantities by standard thermodynamic relations [41], which are presented in Table III.

In the second part, the phase-space functions are related to ensemble averages, which comprise combinations of the instantaneous values of the kinetic energy $K = L + \mu N - $ $U(\mathbf{r}^N)$, where U is the potential energy, volume derivatives of the potential energy $\partial^n U/\partial V^n$, and the number of particles N. To retain clarity, only systems of pure fluids which consist of spherical particles with three translational degrees of freedom are considered in this work. Expressions 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

TABLE III. General relations for important thermodynamic properties.

Isochoric heat capacity	$C_V = \left(\dfrac{\partial E}{\partial T}\right)_{V,N}$
Thermal pressure coefficient	$\gamma_V = \left(\dfrac{\partial p}{\partial T}\right)_{V,N}$
Isothermal compressibility	$\beta_T = -\dfrac{1}{V}\left(\dfrac{\partial V}{\partial p}\right)_{T,N}$
Isobaric thermal expansivity	$\alpha_p = \dfrac{1}{V}\left(\dfrac{\partial V}{\partial T}\right)_{p,N} = \beta_T \gamma_V$
Isobaric heat capacity	$C_p = \left(\dfrac{\partial H}{\partial T}\right)_{p,N} = C_V + VT\beta_T\gamma_V^2$
Isentropic compressibility	$\beta_S = -\dfrac{1}{V}\left(\dfrac{\partial V}{\partial p}\right)_{S,N} = \beta_T \dfrac{C_V}{C_p}$
Speed of sound	$w^2 = -\dfrac{V^2}{NM}\left(\dfrac{\partial p}{\partial V}\right)_{S,N} = \dfrac{V}{NM\beta_S}$
Joule–Thomson coefficient	$\mu_{\mathrm{JT}} = \left(\dfrac{\partial T}{\partial p}\right)_{H,N} = \dfrac{V}{C_p}(T\alpha_p - 1)$

number of degrees of freedom of one molecule. The generalization to mixtures is also straightforward and therefore not pursued here.

For systems of spherical particles, the phase-space volume of the μVL ensemble is given by Eq. (1). If the potential energy is a function of the particle coordinates only, the energy E can be separated into the kinetic energy $K = \sum \mathbf{p}_i^2/2m$ and the potential energy. The integrals over the momenta of the particles can be evaluated by the Laplace transformation technique originally developed by Pearson *et al.* [35] for the microcanonical ensemble. Moreover, to remove the dependence of the integral over the particle coordinates on volume, the coordinates are transformed into dimensionless coordinates $\mathbf{r}'$ by $\mathbf{r}' = V^{-1/3}\mathbf{r}$. This yields

$$\Omega(\mu, V, L) = \sum_{N=0}^{\infty} \frac{1}{N!h^{3N}} \frac{(2\pi m)^{\frac{3N}{2}}}{\Gamma\left(\frac{3N}{2}+1\right)} \int V^N (L+\mu N - U)^{\frac{3N}{2}}$$
$$\times \Theta(L+\mu N - U)d\mathbf{r}'^N, \tag{26}$$

in which $\Gamma(x)$ represents the gamma function. In a similar manner, the phase-space density is transformed into

$$\omega(\mu, V, L) = \sum_{N=0}^{\infty} \frac{1}{N!h^{3N}} \frac{(2\pi m)^{\frac{3N}{2}}}{\Gamma\left(\frac{3N}{2}\right)} \int V^N (L+\mu N - U)^{\frac{3N}{2}-1}$$
$$\times \Theta(L+\mu N - U)d\mathbf{r}'^N, \tag{27}$$

where the recurrence relation for the gamma function $\Gamma(x+1) = x\Gamma(x)$ has been used.

The ensemble average of an arbitrary quantity $A(\mathbf{r}^N, \mathbf{p}^N)$ is defined by

$$\langle A \rangle = \frac{1}{\omega} \sum_{N=0}^{\infty} \frac{1}{N!h^{3N}} \iint A(\mathbf{r}^N, \mathbf{p}^N)\delta(L+\mu N - \mathcal{H})d\mathbf{r}^N d\mathbf{p}^N. \tag{28}$$

Since the potential energy depends only on the coordinates of the particles and $K = L + \mu N - U(\mathbf{r}^N)$, the kinetic energy can be considered as a function of the particle coordinates only. Therefore, the instantaneous values of an arbitrary property A also depend on the particle coordinates only. Consequently, the Laplace transform technique can be applied to evaluate the integrals over the momenta of the particles in Eq. (28), which results in

$$\langle A \rangle = \frac{1}{\omega} \sum_{N=0}^{\infty} \frac{1}{N!h^{3N}} \frac{(2\pi m)^{\frac{3N}{2}}}{\Gamma\left(\frac{3N}{2}\right)} \int A(\mathbf{r}'^N)V^N$$
$$\times (L+\mu N - U)^{\frac{3N}{2}-1}\Theta(L+\mu N - U)d\mathbf{r}'^N. \tag{29}$$

Expressions for phase-space functions Ω_{mno} in terms of ensemble averages can now be derived by calculating derivatives of the phase-space volume, Eq. (26), multiplying the result by the inverse phase-space density, and comparing it to the general equation for an ensemble average, Eq. (29). For instance, the phase-space function Ω_{000} can be written as

$$\Omega_{000} = \frac{\Omega}{\omega} = \frac{1}{\omega} \sum_{N=0}^{\infty} \frac{1}{N!h^{3N}} \frac{(2\pi m)^{\frac{3N}{2}}}{\Gamma\left(\frac{3N}{2}\right)\frac{3N}{2}}$$
$$\times \int V^N (L+\mu N - U)^{\frac{3N}{2}}\Theta(L+\mu N - U)d\mathbf{r}'^N. \tag{30}$$

Comparing Eq. (30) to Eq. (29) yields

$$\Omega_{000} = \left\langle \left(\frac{3N}{2}\right)^{-1}(L+\mu N - U)\right\rangle. \tag{31}$$

Due to the definition of the phase-space functions by Eq. (7), Ω_{100} is unity because the derivative of the phase-space volume with respect to the Hill energy is the phase-space density.

Analogously, an expression for the phase-space function related to the partial derivative of the phase-space volume with respect to volume Ω_{010} is obtained as

$$\Omega_{010} = \frac{1}{\omega}\frac{\partial \Omega}{\partial V} = \frac{1}{\omega} \sum_{N=0}^{\infty} \frac{1}{N!h^{3N}} \frac{(2\pi m)^{\frac{3N}{2}}}{\Gamma\left(\frac{3N}{2}\right)\frac{3N}{2}} \int NV^{N-1}(L+\mu N - U)^{\frac{3N}{2}}\Theta(L+\mu N - U)d\mathbf{r}'^N$$
$$+ \frac{1}{\omega} \sum_{N=0}^{\infty} \frac{1}{N!h^{3N}} \frac{(2\pi m)^{\frac{3N}{2}}}{\Gamma\left(\frac{3N}{2}\right)} \int V^N (L+\mu N - U)^{\frac{3N}{2}-1}\left(-\frac{\partial U}{\partial V}\right)\Theta(L+\mu N - U)d\mathbf{r}'^N. \tag{32}$$

The comparison with Eq. (29) results in

$$\Omega_{010} = \frac{2}{3V}\langle L+\mu N - U\rangle - \left\langle \frac{\partial U}{\partial V}\right\rangle = \frac{2}{3V}\langle K\rangle - \left\langle \frac{\partial U}{\partial V}\right\rangle. \tag{33}$$

The expression exhibits the same structure as the equations for the pressure in the microcanonical, canonical, and grand-canonical ensembles [28,31,32]. The first term is the ideal gas part of the pressure, while the ensemble average of the derivative of the potential energy with respect to volume in the second term describes the residual contribution to the pressure.

The phase-space function Ω_{001}, which is related to the first derivative of the phase-space volume with respect to the chemical potential, is

$$\Omega_{001} = \frac{1}{\omega}\frac{\partial\Omega}{\partial\mu} = \frac{1}{\omega}\sum_{N=0}^{\infty}\frac{1}{N!h^{3N}}\frac{(2\pi m)^{\frac{3N}{2}}}{\Gamma\left(\frac{3N}{2}\right)}\int V^N (L+\mu N-U)^{\frac{3N}{2}-1} N\,\Theta(L+\mu N-U)d\mathbf{r}'^N. \tag{34}$$

Comparing it with Eq. (29) yields the simple result

$$\Omega_{001} = \langle N\rangle. \tag{35}$$

In the same way, further expressions for phase-space functions of higher and mixed order can be obtained. The expressions for phase-space functions up to third order are listed in Table IV.

By mathematical induction, a general expression for the phase-space functions of arbitrary order,

$$\Omega_{mno} = \left\langle \left(\frac{N}{V}\right)^n N^o\left[\mathcal{P}_n^{-N}\mathcal{P}_{m+o}^{-3N/2}\left(\frac{L+\mu N-U}{3N/2}\right)^{1-m-o}\right.\right.$$
$$\left.\left. + (1-\delta_{0n})\sum_{i=1}^n\binom{n}{i}\mathcal{P}_{n-i}^{-N}\sum_{l=1}^i\mathcal{P}_{m+l+o}^{-3N/2}\frac{1}{N^{i-l}}\left(\frac{L+\mu N-U}{3N/2}\right)^{1-m-l-o}\sum_{k=1}^{k_{\max}(i,l)}c_{ilk}\frac{V^i\mathcal{W}_{ilk}}{N^l}\right]\right\rangle, \tag{36}$$

can be established. The symbol $\mathcal{P}_x^X$ denotes the Pochhammer polynomials [42], which were defined by Lustig as [30]

$$\mathcal{P}_x^X = \begin{cases} 1, & \text{for } x=0 \text{ or } x=1,\\ \left(1+\frac{1}{X}\right)...\left(1+\frac{x-1}{X}\right), & \text{otherwise.} \end{cases} \tag{37}$$

and δ_{ij} is the Kronecker δ defined by $\delta_{ij}=1$ if $i=j$ and $\delta_{ij}=0$ if $i\neq j$.

The structure of the terms $c_{ilk}\mathcal{W}_{ilk}$ in Eq. (36) can be described by multinomials on the basis of combinatorial analysis. A multinomial coefficient

$$c_{ilk} = \frac{i!}{a_1!(1!)^{a_1}a_2!(2!)^{a_2}\ldots a_i!(i!)^{a_i}} \tag{38}$$

is the number of ways of partitioning a set of

$$i = a_1 + 2a_2 + \ldots + ia_i \tag{39}$$

objects into a_1 subsets containing one object, a_2 subsets containing two objects, ..., a_i subsets containing i objects [43]. In other words, one looks for all possible solutions to Eq. (39). Each solution yields the structure of one term $c_{ilk}\mathcal{W}_{ilk}$ for a given triplet (i,l,k). Each $\mathcal{W}_{ilk}$ is a product of various powers of negative volume derivatives of the potential energy $-\partial^n U/\partial V^n$. A derivative of order n occurs a_n times as a factor in this product. The index $l=a_1+a_2+\ldots+a_i$ in c_{ilk} and $\mathcal{W}_{ilk}$ corresponds to the number of factors in the product, and i is the sum of the orders of the derivatives in one term. For some l there are several different solutions to Eq. (39), which are enumerated by k, and $k_{\max}(i,l)$ is the number of solutions for a given pair of i and l, i.e., the degeneracy. With this background, the correspondences between the combinatorial problem and the structure of the terms become clear. The i objects are the orders of derivatives to be partitioned into subsets; i.e., each object corresponds to one order of derivative, n is the order of a derivative in a subset, and the number of

subsets a_n corresponds to the number of times the derivative occurs in this term as a factor, i.e., a_n is the exponent of the derivative.

To illustrate the construction of a term $c_{ilk}\mathcal{W}_{ilk}$, it is instructive to consider an example. For $i=2$ there are two possible solutions to Eq. (39), for $(l=1,k=1)$ $1\times 0 + \underline{2\times 1} = 2$, which yields the term $-\partial^2 U/\partial V^2$ and $c_{211}=1$, and for $(l=2,k=1)$ $\underline{1\times 2} + 2\times 0 = 2$, which yields $(-\partial U/\partial V)^2$ and $c_{221}=1$. A complete list of the first few terms was given by Lustig [24,28] and Meier and Kabelac [34].

III. EXPRESSIONS FOR THERMODYNAMIC PROPERTIES IN THE μpR ENSEMBLE

In the μpR ensemble, also the entropy is the thermodynamic potential, and the independent variables are the chemical potential, the pressure, and the Ray energy R, which is defined by $R=E+pV-\mu N$ and was introduced by Ray [11]. Since the procedure for the derivation of expressions for thermodynamic properties in the μpR ensemble is similar to the one applied in Sec. II to the μVL ensemble and the structure of many equations to be derived in this section resembles that of equations for the μVL ensemble, the description is kept brief when appropriate. The phase-space volume of the μpR ensemble is defined by

$$\Omega(\mu,p,R) = \sum_{N=0}^{\infty}\frac{1}{N!h^{3N}}\int_0^{\infty}\!\!\iint\frac{N}{V}\Theta(R-pV+\mu N-\mathscr{H})$$
$$\times d\mathbf{r}^N d\mathbf{p}^N dV \tag{40}$$

and the phase-space density by

$$\omega(\mu,p,R) = \sum_{N=0}^{\infty}\frac{1}{N!h^{3N}}\int_0^{\infty}\!\!\iint\frac{N}{V}\delta(R-pV+\mu N-\mathscr{H})$$
$$\times d\mathbf{r}^N d\mathbf{p}^N dV. \tag{41}$$

TABLE IV. Expressions for phase-space functions Ω_{mno} up to third order in terms of ensemble averages in the μVL ensemble.

$$\Omega_{000} = \left\langle \left(\frac{3N}{2}\right)^{-1} (L + \mu N - U) \right\rangle$$

$$\Omega_{100} = 1$$

$$\Omega_{200} = \left\langle \left(\frac{3N}{2} - 1\right)(L + \mu N - U)^{-1} \right\rangle$$

$$\Omega_{300} = \left\langle \left(\frac{3N}{2} - 1\right)\left(\frac{3N}{2} - 2\right)(L + \mu N - U)^{-2} \right\rangle$$

$$\Omega_{010} = \frac{2}{3V}\langle L + \mu N - U \rangle - \left\langle \frac{\partial U}{\partial V} \right\rangle$$

$$\Omega_{020} = \left\langle \frac{2(N-1)}{3V^2}(L + \mu N - U) \right\rangle - \left\langle 2\frac{N}{V}\frac{\partial U}{\partial V} \right\rangle + \left\langle \left(\frac{3N}{2} - 1\right)(L + \mu N - U)^{-1}\left(\frac{\partial U}{\partial V}\right)^2 \right\rangle - \left\langle \frac{\partial^2 U}{\partial V^2} \right\rangle$$

$$\Omega_{030} = \left\langle \frac{2(N-1)(N-2)}{3V^3}(L + \mu N - U) \right\rangle - \left\langle 3\frac{N(N-1)}{V^2}\frac{\partial U}{\partial V} \right\rangle - \left\langle 3\frac{N}{V}\frac{\partial^2 U}{\partial V^2} \right\rangle + \left\langle 3\left(\frac{3N}{2} - 1\right)\frac{N}{V}(L + \mu N - U)^{-1}\left(\frac{\partial U}{\partial V}\right)^2 \right\rangle$$
$$+ \left\langle 3\left(\frac{3N}{2} - 1\right)(L + \mu N - U)^{-1}\frac{\partial U}{\partial V}\frac{\partial^2 U}{\partial V^2} \right\rangle - \left\langle \left(\frac{3N}{2} - 1\right)\left(\frac{3N}{2} - 2\right)(L + \mu N - U)^{-2}\left(\frac{\partial U}{\partial V}\right)^3 \right\rangle - \left\langle \frac{\partial^3 U}{\partial V^3} \right\rangle$$

$$\Omega_{001} = \langle N \rangle$$

$$\Omega_{002} = \left\langle \left(\frac{3N}{2} - 1\right)(L + \mu N - U)^{-1}N^2 \right\rangle$$

$$\Omega_{003} = \left\langle \left(\frac{3N}{2} - 1\right)\left(\frac{3N}{2} - 2\right)(L + \mu N - U)^{-2}N^3 \right\rangle$$

$$\Omega_{110} = \left\langle \frac{N}{V} \right\rangle - \left\langle \left(\frac{3N}{2} - 1\right)(L + \mu N - U)^{-1}\frac{\partial U}{\partial V} \right\rangle$$

$$\Omega_{101} = \left\langle \left(\frac{3N}{2} - 1\right)(L + \mu N - U)^{-1}N \right\rangle$$

$$\Omega_{011} = \left\langle \frac{N^2}{V} \right\rangle - \left\langle \left(\frac{3N}{2} - 1\right)(L + \mu N - U)^{-1}\frac{\partial U}{\partial V}N \right\rangle$$

$$\Omega_{120} = \left\langle \frac{N^2 - N}{V^2} \right\rangle - \left\langle 2\frac{N}{V}\frac{\partial U}{\partial V}\left(\frac{3N}{2} - 1\right)(L + \mu N - U)^{-1} \right\rangle + \left\langle \left(\frac{3N}{2} - 1\right)\left(\frac{3N}{2} - 2\right)(L + \mu N - U)^{-2}\left(\frac{\partial U}{\partial V}\right)^2 \right\rangle$$
$$- \left\langle \left(\frac{3N}{2} - 1\right)(L + \mu N - U)^{-1}\frac{\partial^2 U}{\partial V^2} \right\rangle$$

$$\Omega_{210} = \left\langle \frac{N}{V}\left(\frac{3N}{2} - 1\right)(L + \mu N - U)^{-1} \right\rangle - \left\langle \left(\frac{3N}{2} - 1\right)\left(\frac{3N}{2} - 2\right)(L + \mu N - U)^{-2}\frac{\partial U}{\partial V} \right\rangle$$

$$\Omega_{012} = \left\langle \frac{N^3}{V}\left(\frac{3N}{2} - 1\right)(L + \mu N - U)^{-1} \right\rangle - \left\langle \left(\frac{3N}{2} - 1\right)\left(\frac{3N}{2} - 2\right)(L + \mu N - U)^{-2}\frac{\partial U}{\partial V}N^2 \right\rangle$$

$$\Omega_{021} = \left\langle \frac{N^3 - N^2}{V^2} \right\rangle - \left\langle 2\frac{N^2}{V}\frac{\partial U}{\partial V}\left(\frac{3N}{2} - 1\right)(L + \mu N - U)^{-1} \right\rangle + \left\langle \left(\frac{3N}{2} - 1\right)\left(\frac{3N}{2} - 2\right)(L + \mu N - U)^{-2}\left(\frac{\partial U}{\partial V}\right)^2 N \right\rangle$$
$$- \left\langle \left(\frac{3N}{2} - 1\right)(L + \mu N - U)^{-1}\frac{\partial^2 U}{\partial V^2}N \right\rangle$$

$$\Omega_{102} = \left\langle \left(\frac{3N}{2} - 1\right)\left(\frac{3N}{2} - 2\right)(L + \mu N - U)^{-2}N^2 \right\rangle$$

$$\Omega_{201} = \left\langle \left(\frac{3N}{2} - 1\right)\left(\frac{3N}{2} - 2\right)(L + \mu N - U)^{-2}N \right\rangle$$

$$\Omega_{111} = \left\langle \frac{N^2}{V}\left(\frac{3N}{2} - 1\right)(L + \mu N - U)^{-1} \right\rangle - \left\langle \left(\frac{3N}{2} - 1\right)\left(\frac{3N}{2} - 2\right)(L + \mu N - U)^{-2}\frac{\partial U}{\partial V}N \right\rangle$$

Since the volume is not constant, but fluctuates in the μpR ensemble, both phase-space volume and phase-space density include an additional integration over all volumes that are accessible to the system, that is from zero to infinity. This additional integration introduces the unit of volume into the phase-space volume and phase-space density, which must be compensated for by an appropriate volume scale. Han and Son [44] showed that in molecular simulations of homogeneous systems within periodic boundary conditions the factor N/V is an appropriate volume scale. It was already used in the partition functions of the NpT and NpH ensembles in our previous works [31,33] and is therefore also applied here

in the phase-space volume and phase-space density of the μpR ensemble. It should be noted that this volume scale was already derived earlier by Attard using information theory [45]. The volume scale has no influence on the equations for thermodynamic properties, but must be taken into account in the acceptance criterion for volume changes in Metropolis Monte Carlo simulations in the μpR ensemble. Its influence is largest for small systems, but vanishes for large systems in the thermodynamic limit $N \to \infty$.

The entropy can also be defined with the phase-space volume or the phase-space density by Eqs. (3) or (4) as in the μVL ensemble. In the μpR ensemble, the phase-space functions are

defined by

$$\Omega_{mno} = \frac{1}{\omega} \frac{\partial^{m+n+o}\Omega}{\partial R^m \partial p^n \partial \mu^o}, \quad m, n, o = 0, 1, 2, \ldots, \quad (42)$$

with the special case $\Omega_{100} = 1$. The recurrence relations for the space-space functions and the expressions for derivatives of the entropy S_{mno}^{Ω} and S_{mno}^{ω} have the same structure as in the μVL ensemble. They can be obtained from Eqs. (9) to (11) and the equations in Table I by replacing L by R and V by p. The total differential of the entropy $S = S(\mu, p, R)$ is given by [1]

$$dS = \frac{1}{T}dR - \frac{V}{T}dp + \frac{N}{T}d\mu \quad (43)$$

and serves as starting point for deriving expressions of properties that are related to first-order derivatives of the entropy in terms of phase-space functions. Thus, for the inverse temperature the expression

$$T^{-1} = \left(\frac{\partial S}{\partial R}\right)_{p,\mu} = k_B S_{100} \stackrel{\Omega}{=} k_B \Omega_{000}^{-1} \quad (44)$$

is obtained, which leads to

$$T \stackrel{\Omega}{=} k_B^{-1} \Omega_{000}. \quad (45)$$

The volume is related to the derivative of the entropy with respect to pressure by

$$V = -T\left(\frac{\partial S}{\partial p}\right)_{R,\mu} = -Tk_B S_{010} \stackrel{\Omega}{=} -\Omega_{010}, \quad (46)$$

while the number of particles is related to the derivative of the entropy with respect to chemical potential by

$$N = T\left(\frac{\partial S}{\partial \mu}\right)_{R,V} = Tk_B S_{001} \stackrel{\Omega}{=} \Omega_{001}. \quad (47)$$

Equations for the isobaric heat capacity, the isobaric thermal expansivity, and the isothermal compressibility can be found by using the method of Jacobian determinants again. The resulting equations have the same mathematical structure as Eqs. (23)–(25). Thus, the equation for the isobaric heat capacity,

$$C_p = \left(\frac{\partial H}{\partial T}\right)_{p,N} = \frac{\left(\frac{\partial N}{\partial \mu}\right)_{R,p} - N\left(\frac{\partial N}{\partial R}\right)_{p,\mu}}{\left(\frac{\partial T}{\partial R}\right)_{p,\mu}\left(\frac{\partial N}{\partial \mu}\right)_{R,p} - \left(\frac{\partial N}{\partial R}\right)_{p,\mu}\left(\frac{\partial T}{\partial \mu}\right)_{R,p}}, \quad (48)$$

is obtained by replacing the internal energy E by the enthalpy H, the volume V by the pressure p, and the Hill energy L by the Ray energy R in Eq. (23). Similarly, retaining the factor V^{-1}, exchanging the volume V and the pressure p, and replacing the Hill energy L by the Ray energy R in all partial derivatives in Eq. (24) yields the equation for the isobaric thermal expansivity

$$\alpha_p = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_{p,N} = \frac{1}{V} \frac{\left(\frac{\partial V}{\partial R}\right)_{p,\mu}\left(\frac{\partial N}{\partial \mu}\right)_{R,p} - \left(\frac{\partial N}{\partial R}\right)_{p,\mu}\left(\frac{\partial V}{\partial \mu}\right)_{R,p}}{\left(\frac{\partial T}{\partial R}\right)_{p,\mu}\left(\frac{\partial N}{\partial \mu}\right)_{R,p} - \left(\frac{\partial N}{\partial R}\right)_{p,\mu}\left(\frac{\partial T}{\partial \mu}\right)_{R,p}}. \quad (49)$$

Finally, the equation for the thermal compressibility

$$\beta_T = -\frac{1}{V}\left\{\left(\frac{\partial V}{\partial p}\right)_{R,\mu} + \left(\frac{\partial V}{\partial R}\right)_{p,\mu} \frac{\left(\frac{\partial T}{\partial p}\right)_{R,\mu}\left(\frac{\partial N}{\partial \mu}\right)_{R,p} - \left(\frac{\partial T}{\partial \mu}\right)_{R,p}\left(\frac{\partial N}{\partial p}\right)_{R,\mu}}{\left(\frac{\partial N}{\partial R}\right)_{p,\mu}\left(\frac{\partial T}{\partial \mu}\right)_{R,p} - \left(\frac{\partial T}{\partial R}\right)_{p,\mu}\left(\frac{\partial N}{\partial \mu}\right)_{R,p}} + \left(\frac{\partial V}{\partial \mu}\right)_{R,p} \frac{\left(\frac{\partial T}{\partial R}\right)_{p,\mu}\left(\frac{\partial N}{\partial p}\right)_{R,\mu} - \left(\frac{\partial T}{\partial p}\right)_{R,\mu}\left(\frac{\partial N}{\partial R}\right)_{p,\mu}}{\left(\frac{\partial N}{\partial R}\right)_{p,\mu}\left(\frac{\partial T}{\partial \mu}\right)_{R,p} - \left(\frac{\partial T}{\partial R}\right)_{p,\mu}\left(\frac{\partial N}{\partial \mu}\right)_{R,p}}\right\} \quad (50)$$

is obtained by changing the factor V to V^{-1}, exchanging the volume V and the pressure p, and replacing the Hill energy L by the Ray energy R in all partial derivatives in Eq. (25). Since the partial derivatives in the μpR ensemble directly correspond to those in the μVL ensemble, the expressions for the isobaric heat capacity, isobaric thermal expansion coefficient, and isothermal compressibility in terms of phase-space functions in the μpR ensemble correspond to those for the isochoric heat capacity, thermal pressure coefficient, and inverse thermal compressibility in the μVL ensemble. As the resulting expressions are rather lengthy, they are omitted here. For the calculation of thermodynamic properties in the μpR ensemble, a stepwise procedure should be applied as already suggested for the μVL ensemble in Sec. II. Further important thermodynamic properties, which are related to second-order derivatives of the thermodynamic potential, e.g., the isochoric heat capacity, thermal pressure coefficient, isentropic compressibility, speed of sound, and Joule–Thomson coefficient, can be calculated in terms of these three quantities using the results for C_p, α_p, and β_T with the thermodynamic relations listed in Table III.

In the second step, expressions for the phase-space functions in terms of ensemble averages are derived along the same lines as for the μVL ensemble in Sec. II. The integrals over the momenta in the phase-space volume and density are evaluated by the Laplace transform technique of Pearson *et al.* [35]. Moreover, scaled coordinates $\mathbf{r}' = V^{-1/3}\mathbf{r}$ are introduced to remove the dependence of the integrals over the particle coordinates on volume. This leads to the equations

$$\Omega(\mu, p, R) = \sum_{N=0}^{\infty} \frac{N}{N!h^{3N}} \frac{(2\pi m)^{\frac{3N}{2}}}{\Gamma\left(\frac{3N}{2}+1\right)} \int_0^{\infty} \int V^{N-1}(R - pV + \mu N - U)^{\frac{3N}{2}} \Theta(R - pV + \mu N - U)d\mathbf{r}'^N dV \quad (51)$$

for the phase-space volume and

$$\omega(\mu, p, R) = \sum_{N=0}^{\infty} \frac{N}{N!h^{3N}} \frac{(2\pi m)^{\frac{3N}{2}}}{\Gamma\left(\frac{3N}{2}\right)} \int_0^{\infty} \int V^{N-1}(R - pV + \mu N - U)^{\frac{3N}{2}-1} \Theta(R - pV + \mu N - U)d\mathbf{r}'^N dV \quad (52)$$

for the phase-space density. The equation for an ensemble average of an arbitrary quantity A after evaluation of the integrals over the momenta and introduction of scaled coordinates reads

$$\langle A \rangle = \frac{1}{\omega} \sum_{N=0}^{\infty} \frac{N}{N!h^{3N}} \frac{(2\pi m)^{\frac{3N}{2}}}{\Gamma\left(\frac{3N}{2}\right)} \int A(\mathbf{r}'^N) V^{N-1} (R - pV + \mu N - U)^{\frac{3N}{2}-1} \Theta(R - pV + \mu N - U) d\mathbf{r}'^N. \tag{53}$$

Now the expressions for the phase-space functions can be found by inserting derivatives of the phase-space volume, Eq. (51), into the definition of the phase-space functions, Eq. (7), and comparing the result to Eq. (53). The phase-space function $\Omega_{000} = \Omega/\omega$ is formed by dividing Eq. (51) by ω, which leads to

$$\Omega_{000} = \frac{\Omega}{\omega} = \frac{1}{\omega} \sum_{N=0}^{\infty} \frac{N}{N!h^{3N}} \frac{(2\pi m)^{\frac{3N}{2}}}{\Gamma\left(\frac{3N}{2}\right)\frac{3N}{2}} \int_0^{\infty} \int V^{N-1} (R - pV + \mu N - U)^{\frac{3N}{2}} \Theta(R - pV + \mu N - U) d\mathbf{r}'^N dV. \tag{54}$$

The comparison with Eq. (53) yields

$$\Omega_{000} = \left\langle \left(\frac{3N}{2}\right)^{-1} (R - pV + \mu N - U) \right\rangle. \tag{55}$$

Similarly, the phase-space functions corresponding to the first derivatives of the phase-space volume with respect to pressure and chemical potential are obtained as

$$\Omega_{010} = \frac{1}{\omega} \sum_{N=0}^{\infty} \frac{N}{N!h^{3N}} \frac{(2\pi m)^{\frac{3N}{2}}}{\Gamma\left(\frac{3N}{2}\right)} \int_0^{\infty} \int V^{N-1} (R - pV + \mu N - U)^{\frac{3N}{2}-1} (-V) \Theta(R - pV + \mu N - U) d\mathbf{r}'^N dV \tag{56}$$

and

$$\Omega_{001} = \frac{1}{\omega} \sum_{N=0}^{\infty} \frac{N}{N!h^{3N}} \frac{(2\pi m)^{\frac{3N}{2}}}{\Gamma\left(\frac{3N}{2}\right)} \int_0^{\infty} \int V^{N-1} (R - pV + \mu N - U)^{\frac{3N}{2}-1} N \, \Theta(R - pV + \mu N - U) d\mathbf{r}'^N dV. \tag{57}$$

Hence,

$$\Omega_{010} = -\langle V \rangle \tag{58}$$

and

$$\Omega_{001} = \langle N \rangle. \tag{59}$$

Further expressions for phase-space functions corresponding to partial derivatives of the phase-space volume up to third order are summarized in Table V.

Finally, a general equation for phase-space functions of arbitrary order can be established. In the μpR ensemble, it is given by

$$\Omega_{mno} = \left\langle \mathcal{P}_{m+n+o}^{-3N/2} \left(\frac{R - pV + \mu N - U}{3N/2}\right)^{1-m-n-o} (-V)^n N^o \right\rangle, \tag{60}$$

where the symbol $\mathcal{P}_x^X$ denotes the Pochhammer polynomials defined by Eq. (37). The structure of the phase-space functions in the μpR ensemble is much simpler than that of the corresponding functions in the μVL ensemble because here not the volume, but the pressure is an independent variable. Consequently, no derivatives of the potential energy with respect to volume appear in the expressions for the phase-space functions.

IV. VALIDATION BY MONTE CARLO SIMULATIONS OF A MODEL FLUID

The expressions for thermodynamic properties derived in Secs. II and III were validated by Monte Carlo simulations

of the simple Lennard-Jones model fluid at three state points in both ensembles. We applied the Metropolis Monte Carlo algorithm [46] as modified by Ray [47] for simulations in adiabatic ensembles. In general, a Monte Carlo move from an old state m to a new state n in the Metropolis algorithm is accepted with the probability

$$P_{nm} = \min\left(1, \frac{W_n}{W_m}\right), \tag{61}$$

where W denotes the weight factor of the ensemble. The weight factor can be inferred from the phase-space density ω of the ensemble, which is the normalization factor of the weight factor.

The weight factor of the μVL ensemble is given by

$$W = \frac{1}{N!h^{3N}} \frac{(2\pi m)^{\frac{3N}{2}}}{\Gamma\left(\frac{3N}{2}\right)} V^N (L + \mu N - U)^{\frac{3N}{2}-1} \Theta(L + \mu N - U). \tag{62}$$

In the μVL ensemble, the Markov chain consists of a random sequence of three different types of trials: particle displacements, particle insertions, and particle deletions. In analogy to particle displacements in the microcanonical and NpH ensembles [33,47], the ratio of the weight factors in Eq. (61) for a particle displacement reads

$$\frac{W_n}{W_m} = \left(\frac{L + \mu N - U_n}{L + \mu N - U_m}\right)^{\frac{3N}{2}-1}. \tag{63}$$

TABLE V. Expressions for phase-space functions Ω_{mno} up to third order in terms of ensemble averages in the μpR ensemble.

$$\Omega_{000} = \left\langle \left(\frac{3N}{2}\right)^{-1}(R - pV + \mu N - U)\right\rangle$$

$$\Omega_{100} = 1$$

$$\Omega_{200} = \left\langle \left(\frac{3N}{2} - 1\right)(R - pV + \mu N - U)^{-1}\right\rangle$$

$$\Omega_{300} = \left\langle \left(\frac{3N}{2} - 1\right)\left(\frac{3N}{2} - 2\right)(R - pV + \mu N - U)^{-2}\right\rangle$$

$$\Omega_{010} = -\langle V\rangle$$

$$\Omega_{020} = \left\langle \left(\frac{3N}{2} - 1\right)(R - pV + \mu N - U)^{-1}V^2\right\rangle$$

$$\Omega_{030} = -\left\langle \left(\frac{3N}{2} - 1\right)\left(\frac{3N}{2} - 2\right)(R - pV + \mu N - U)^{-2}V^3\right\rangle$$

$$\Omega_{001} = \langle N\rangle$$

$$\Omega_{002} = \left\langle \left(\frac{3N}{2} - 1\right)(R - pV + \mu N - U)^{-1}N^2\right\rangle$$

$$\Omega_{003} = \left\langle \left(\frac{3N}{2} - 1\right)\left(\frac{3N}{2} - 2\right)(R - pV + \mu N - U)^{-2}N^3\right\rangle$$

$$\Omega_{110} = -\left\langle \left(\frac{3N}{2} - 1\right)(R - pV + \mu N - U)^{-1}V\right\rangle$$

$$\Omega_{101} = \left\langle \left(\frac{3N}{2} - 1\right)(R - pV + \mu N - U)^{-1}N\right\rangle$$

$$\Omega_{011} = -\left\langle \left(\frac{3N}{2} - 1\right)(R - pV + \mu N - U)^{-1}VN\right\rangle$$

$$\Omega_{120} = \left\langle \left(\frac{3N}{2} - 1\right)\left(\frac{3N}{2} - 2\right)(R - pV + \mu N - U)^{-2}V^2\right\rangle$$

$$\Omega_{210} = -\left\langle \left(\frac{3N}{2} - 1\right)\left(\frac{3N}{2} - 2\right)(R - pV + \mu N - U)^{-2}V\right\rangle$$

$$\Omega_{012} = -\left\langle \left(\frac{3N}{2} - 1\right)\left(\frac{3N}{2} - 2\right)(R - pV + \mu N - U)^{-2}VN^2\right\rangle$$

$$\Omega_{021} = \left\langle \left(\frac{3N}{2} - 1\right)\left(\frac{3N}{2} - 2\right)(R - pV + \mu N - U)^{-2}V^2N\right\rangle$$

$$\Omega_{102} = \left\langle \left(\frac{3N}{2} - 1\right)\left(\frac{3N}{2} - 2\right)(R - pV + \mu N - U)^{-2}N^2\right\rangle$$

$$\Omega_{201} = \left\langle \left(\frac{3N}{2} - 1\right)\left(\frac{3N}{2} - 2\right)(R - pV + \mu N - U)^{-2}N\right\rangle$$

$$\Omega_{111} = -\left\langle \left(\frac{3N}{2} - 1\right)\left(\frac{3N}{2} - 2\right)(R - pV + \mu N - U)^{-2}VN\right\rangle$$

Accordingly, the ratios of the weight factor for the insertion or deletion of a particle are given by

$$\frac{W_n}{W_m} = \frac{V(2\pi m)^{3/2}}{(N+1)h^3}\frac{\Gamma\left(\frac{3N}{2}\right)}{\Gamma\left(\frac{3N+3}{2}\right)}\frac{[L + \mu(N+1) - U_n]^{\frac{3N+3}{2}-1}}{(L + \mu N - U_m)^{\frac{3N}{2}-1}} \tag{64}$$

and

$$\frac{W_n}{W_m} = \frac{Nh^3}{V(2\pi m)^{3/2}}\frac{\Gamma\left(\frac{3N}{2}\right)}{\Gamma\left(\frac{3N-3}{2}\right)}\frac{[L + \mu(N-1) - U_n]^{\frac{3N-3}{2}-1}}{(L + \mu N - U_m)^{\frac{3N}{2}-1}}, \tag{65}$$

respectively.

The Markov chain of a Monte Carlo simulation in the μpR ensemble consists of a random sequence of four types of moves. In addition to particle displacements, particle insertions, and particle deletions, volume changes form the fourth type of trial. The acceptance criteria for particle displacements, particle insertions, and particle deletions can be adopted from those for the μVL ensemble by replacing L with $R - pV$ in Eqs. (63) to (65). The ratio of the weight factors for a volume change can be inferred from Eq. (52) and reads

$$\frac{W_n}{W_m} = \left(\frac{V_n}{V_m}\right)^{N-1}\left(\frac{R - pV_n + \mu N - U_n}{R - pV_m + \mu N - U_m}\right)^{\frac{3N}{2}-1}. \tag{66}$$

In contrast to the acceptance criterium for volume changes used by other authors [12,22], where the ratio $(V_n/V_m)^N$ appears instead of $(V_n/V_m)^{N-1}$, the volume scale introduced in Sec. II reduces the exponent N of the ratio by unity. In the thermodynamic limit $N \to \infty$, this difference vanishes, but it must be taken into account when small systems are simulated.

A Fortran 90 software for Monte Carlo simulations in the μVL and μpR ensembles was developed from the codes used in our previous works on the NpT ensemble [31], the grand-canonical ensemble [32], and NpH ensemble [33], which are based on code segments published as attachments to the book of Allen and Tildesley [48].

Since the implementation of the acceptance criteria for particle insertions and deletions might cause numerical problems, some hints for their implementation are in place. To avoid raising a large number to a power of the order of the number of particles, it is useful to transform the ratios of the kinetic energies in the acceptance criteria. For example, in the criterion for the insertion of a particle in the μVL ensemble, the ratio of the kinetic energies can be transformed into

$$\frac{[L + \mu(N+1) - U_n]^{\frac{3N+3}{2}-1}}{[L + \mu N - U_m]^{\frac{3N}{2}-1}}$$
$$= \left[\frac{L + \mu(N+1) - U_n}{L + \mu N - U_m}\right]^{\frac{3N}{2}-1}[L + \mu(N+1) - U_n]^{\frac{3}{2}}. \tag{67}$$

In the transformed expression, the ratio of the kinetic energies in the square brackets is close to unity, and the kinetic energy in the second parentheses is risen only to the power of $3/2$. Before evaluating the acceptance criterion, it must be checked if the kinetic energy $K_n = L + \mu(N+1) - U_n$ of the new configuration is negative. In this case, the trial move must be discarded without evaluation of the acceptance criterion.

Moreover, to avoid the evaluation of the gamma function for large arguments, the recurrence formula $\Gamma(x+1) = x\Gamma(x)$ and Stirling's approximation

$$\Gamma(z) = \sqrt{\frac{2\pi}{z}}\left(\frac{z}{e}\right)^z[1 + \mathcal{O}(z^{-1})] \tag{68}$$

can be applied [49]. Applying these relations to the ratio of the gamma functions in Eq. (64) yields

$$\frac{\Gamma\left(\frac{3N}{2}\right)}{\Gamma\left(\frac{3N+3}{2}\right)} = \frac{2}{3N+1}\left(\frac{3N}{3N+1}\right)^{\frac{3N}{2}}\sqrt{\frac{2e}{3N}}, \tag{69}$$

the numerical evaluation of which provides no problem because the ratio $3N/(3N + 1)$ is always close to unity. In a similar manner, the acceptance criterion for a particle deletion can be modified.

In the remainder of this section, all symbols represent dimensionless quantities in the usual Lennard-Jones dimensionless quantity system, in which all quantities are reduced by the length parameter σ and well depth ε of the Lennard-Jones potential, which is given by

$$u(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right], \tag{70}$$

where r is the distance between a pair of particles. The reduced quantities are defined by $T^* = Tk_{\mathrm{B}}/\varepsilon$, $p^* = p\sigma^3/\varepsilon$, $\rho^* = \rho\sigma^3$, $E^* = E/\varepsilon$, $H^* = H/\varepsilon$, $L^* = L/\varepsilon$, $R^* = R/\varepsilon$, $C_V^* = C_V/k_{\mathrm{B}}$, $C_p^* = C_p/k_{\mathrm{B}}$, $\gamma_V^* = \gamma_V\sigma^3/k_{\mathrm{B}}$, $\alpha_p^* = \alpha_p k_{\mathrm{B}}/\varepsilon$, $\beta_T^* = \beta_T\sigma^3/\varepsilon$, $\beta_S^* = \beta_S\sigma^3/\varepsilon$, $w^* = w(NM/\varepsilon)^{1/2}$, 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.

For both ensembles, simulations were carried out at three characteristic state points. For the simulations in the μVL ensemble, the state points ($\mu = -7.65$, $V = 60\,000$, $L = 26\,244$) in the gas region, ($\mu = -5.3$, $V = 3750$, $L = 3645$) in the liquid region, and ($\mu = -12.0$, $V = 5000$, $L = 37\,908$) in the supercritical region were chosen. For the simulations in the μpR ensemble, the state points ($\mu = -7.65$, $p = 0.05$, $R = 29\,160$) in the gas region, ($\mu = -5.3$, $p = 1.0$, $R = 7290$) in the liquid region, and ($\mu = -12$, $p = 3.0$, $R = 53\,946$) in the supercritical region were selected. The values of the independent variables for the simulations were calculated with the empirical Thol *et al.* equation of state (EOS) [50] for the Lennard-Jones model fluid and chosen such that approximately the same states are simulated in the gas, liquid, and supercritical regions in both ensembles.

As is common practice in empirical equations of state, the zero points of the enthalpy and entropy of the EOS are defined according to conventions in a particular industry or in accordance with recommendations of the IUPAC [51]. In the Thol *et al.* EOS, the state ($T_0 = 0.8$, $p_0 = 0.001$) was chosen as reference state such that the enthalpy and entropy of the ideal gas are zero at this state and the corresponding density of the ideal gas $\rho_0 = p_0/T_0$ [50]. However, since the ideal gas parts of the chemical potential, Hill energy, and Ray energy do not cancel in the acceptance criteria for particle insertions and deletions in simulations in the μVL and μpR ensembles, their prescribed values must be consistent with the statistical-mechanical convention for the enthalpy and entropy of the ideal gas [40]. The adaption of the enthalpy and entropy of the ideal gas of the EOS in the reference state to the statistical-mechanical convention is described in detail in the Appendix.

All simulations were carried out in a cubic simulation box under the usual periodic boundary conditions and minimum image convention. They were performed with 2916 particles and started from a cubic face-centered lattice configuration. The number of particle was chosen rather large to obtain simulation results that are close to the values in the thermodynamic limit.

The Markov chain of each simulation was divided into cycles. Each cycle comprised N trials, where N changed during the simulation due to particle insertions and deletions. Each simulation comprised an equilibration phase of 10^5 cycles and a production phase of 2×10^7 cycles. To fulfill the condition of detailed balance, the type of trial was chosen randomly by a random number generated from a uniform distribution in the interval [0, 1]. Random numbers were generated throughout all simulations with the random number generator ran2 [52]. In the μVL ensemble, the Markov chain consists of particle displacements, particle deletions, and particle insertions. If the random number was smaller than $1/N$, a change in particle number, otherwise a particle displacement was attempted. If the former was chosen, a second random number was generated. If the second random number was smaller than 0.5, a particle deletion, otherwise a particle insertion was attempted. If a deletion was attempted, the particle to be deleted was chosen by a third random number. For a particle insertion, the new particle was inserted at a random position in the cubic box. If a particle displacement was attempted, a second random number was generated to determine the particle to be displaced.

In the μpR ensemble, the Markov chain additionally contains trials of volume changes. If the first random number was smaller than $1/N$, a change in particle number was attempted as described for the μVL ensemble. If the random number was larger than $1 - 1/N$, a volume change was attempted. Otherwise, a particle displacement was attempted.

In all simulations, the cutoff radius was set to half the box length. To account for interactions between pairs of particles whose distance is larger than the cutoff radius, a long-range correction for the potential energy and in the μVL ensemble also for derivatives of the potential with respect to volume was applied as described by Lustig [29] and Meier and Kabelac [34]. When a particle was inserted or deleted or the volume was changed in the μpR ensemble, the cutoff radius and the long-range corrections were adapted. The uncertainty of the simulation results was estimated by the standard block method.

The application of the equations derived in Secs. II and III for the calculation of thermodynamic properties in a Monte Carlo simulation is straightforward. During the production phase of the simulation, the instantaneous values of all combinations of quantities which are required to calculate the phase-space functions of the μVL ensemble in Table IV and of the μpR ensemble in Table V are accumulated after each cycle. After the production phase has been completed, ensemble averages, and with them the phase-space functions, are calculated. The thermodynamic properties can then be obtained using the equations in Table II for the temperature, pressure or volume, average particle number, and their derivatives with respect to Hill or Ray energy, volume or pressure, and chemical potential. These results are used to calculate the isochoric heat capacity, the thermal pressure coefficient, and the isothermal compressibility by Eqs. (23)–(25) in the μVL ensemble or the isobaric heat capacity, isobaric thermal expansivity, and isothermal compressibility by Eqs. (48), (49), and (50) in the μpR ensemble, respectively. Further properties are then calculated by the thermodynamic relations provided in Table III. In both ensembles, all thermodynamic properties were calculated for both entropy definitions.

TABLE VI. Monte Carlo simulation results for the μVL ensemble, their expanded uncertainty (at the 0.95 confidence level), and values calculated with the empirical equation of state of Thol *et al.* [50] for 14 thermodynamic properties at three state points of the Lennard-Jones model fluid using both entropy definitions $S = k_B \ln \Omega$ and $S = k_B \ln \omega$. The production phase of each simulation comprised 2×10^7 cycles. The values of the equation of state were calculated with the simulation results for the temperature and density. The numbers in parentheses denote expanded uncertainties (at the 0.95 confidence level) in the rightmost digits, i.e., 1.516(6) means that the value 1.516 has an expanded uncertainty of 0.006.

Property	Gas $\mu = -7.65, V = 60000, L = 26244$		Liquid $\mu = -5.3, V = 3750$ $L = 3645$		Supercritical $\mu = -12.0, V = 5000,$ $L = 37908$	
	Simulation	EOS	Simulation	EOS	Simulation	EOS
			$S = k_B \ln \Omega$			
N	2906.43(6)		3007.1(5)		2820.0(5)	
T	1.19236(9)	1.19236	0.98185(26)	0.98185	3.0749(10)	3.0749
ρ	0.0484405(20)	0.0484405	0.80190(14)	0.80190	0.56399(10)	0.56399
p	0.047261(9)	0.047256	0.9702(34)	0.9635	3.19070(25)	3.19162
E/N	1.37974(36)	1.37996	$-4.08786(21)$	-4.08911	1.4431(24)	1.4408
H/N	2.3555(6)	2.3555	$-2.8783(39)$	-2.8876	7.1007(38)	7.0998
C_V/N	1.7072(17)	1.7032	2.3992(20)	2.3899	1.82206(39)	1.82410
C_p/N	3.807(9)	3.793	4.863(26)	4.822	3.490(8)	3.488
γ_V	0.056266(47)	0.056211	4.935(10)	4.922	1.5473(14)	1.5455
α_p	1.516(6)	1.511	0.4078(32)	0.4035	0.1977(7)	0.1975
β_T	26.95(10)	26.87	0.08262(48)	0.08198	0.12777(38)	0.12778
β_S	12.083(21)	12.067	0.04076(6)	0.04063	0.06671(6)	0.06682
w	1.3071(11)	1.3080	5.5312(40)	5.5398	5.1554(23)	5.1511
μ_{JT}	4.380(27)	4.360	$-0.1538(15)$	-0.1562	$-0.1992(16)$	-0.1997
			$S = k_B \ln \omega$			
N	2906.58(12)		3007.1(5)		2820.1(5)	
T	1.19234(18)	1.19234	0.98195(26)	0.98195	3.0752(10)	3.0752
ρ	0.0484430(19)	0.0484430	0.80188(14)	0.80188	0.56402(10)	0.56402
p	0.047261(9)	0.047257	0.9704(34)	0.9637	3.19156(25)	3.19248
E/N	1.37974(36)	1.37992	$-4.08786(21)$	-4.08875	1.4431(24)	1.4412
H/N	2.3554(6)	2.3554	$-2.8783(39)$	-2.8870	7.1007(38)	7.1015
C_V/N	1.7068(17)	1.7032	2.3988(20)	2.3898	1.82172(39)	1.82412
C_p/N	3.807(9)	3.794	4.863(26)	4.822	3.489(8)	3.488
γ_V	0.056270(47)	0.056214	4.935(10)	4.922	1.5474(14)	1.5456
α_p	1.516(6)	1.511	0.4077(32)	0.4035	0.1976(7)	0.1974
β_T	26.95(10)	26.87	0.08262(48)	0.08199	0.12773(38)	0.12774
β_S	12.082(21)	12.066	0.04076(6)	0.04064	0.06669(6)	0.06681
w	1.3071(14)	1.3080	5.5314(39)	5.5398	5.1562(17)	5.1516
μ_{JT}	4.381(27)	4.361	$-0.1538(15)$	-0.1562	$-0.1993(16)$	-0.1997

The results of the simulations in the μVL ensemble and μpR ensemble and their uncertainties (at the 0.95 confidence level) are reported in Tables VI and VII, respectively. The first result to note is that the values calculated using the entropy definitions with the phase-space volume or phase-space density agree with each other within their mutual uncertainties. Moreover, the uncertainty of the values obtained for both entropy definitions is very similar. Similar observations were made in our previous work on the *NpH* ensemble. In that work, simulations for the Lennard-Jones model fluid were carried out with different particle numbers for both entropy definitions and the results were extrapolated to the thermodynamic limit. The results for both entropy definitions in the thermodynamic limit agreed well within their uncertainty. Thus, the equations for both entropy definitions are equally well suitable for the calculation of thermodynamic properties in the μVL and μpR ensembles if the number of particles is chosen large enough or simulation results obtained for

different particle numbers are extrapolated to the thermodynamic limit.

In the remainder of this section, we compare our simulation results with the empirical EOS by Thol *et al.* [50], which has been shown by Stephan *et al.* [53] to be among the most accurate representations of the properties of the Lennard-Jones model fluid. According to Thol *et al.* [50], the uncertainty of the EOS in density amounts to 0.1% in the liquid region, 1.0% in the gas region, and 0.15–0.3% in the supercritical region. For other properties, it is 0.5% in the isochoric heat capacity, 1.0% in the isobaric heat capacity, speed of sound, and thermal pressure coefficient, 2.5%–10% in the Joule–Thomson coefficient, 3% in the isothermal compressibility, and 15% in the isobaric thermal expansivity. In the μVL ensemble, the EOS was evaluated with the simulation results for the temperature and density, whereas in the μpR ensemble the prescribed pressure and simulation result for the temperature were used.

TABLE VII. Monte Carlo simulation results for the μpR ensemble, their expanded uncertainty (at the 0.95 confidence level), and values calculated with the empirical equation of state of Thol *et al.* [50] for 13 thermodynamic properties at three state points of the Lennard-Jones model fluid using both entropy definitions $S = k_B \ln \Omega$ and $S = k_B \ln \omega$. The production phase of each simulation comprised 2×10^7 cycles. The values of the equation of state were calculated with the prescribed pressure and the simulation result for the temperature. The numbers in parentheses denote expanded uncertainties (at the 0.95 confidence level) in the rightmost digits, i.e., 1.574(8) means that the value 1.574 has an expanded uncertainty of 0.008.

Property	Gas $\mu = -7.65$, $p = 0.05$, $R = 29160$		Liquid $\mu = -5.3$, $p = 1.0$, $R = 7290$		Supercritical $\mu = -12.0$, $p = 3.0$, $R = 53946$	
	Simulation	EOS	Simulation	EOS	Simulation	EOS
			$S = k_B \ln \Omega$			
N	2922.41(21)		2996.2(1.2)		2870.9(6)	
T	1.19736(17)	1.19736	0.97975(21)	0.97975	3.0245(12)	3.0245
ρ	0.051706(15)	0.051673	0.80463(6)	0.80495	0.55575(13)	0.55545
E/N	1.36071(47)	1.36133	$-4.1095(9)$	-4.1124	1.3925(28)	1.3915
H/N	2.3283(7)	2.3290	$-2.8667(10)$	-2.8701	6.7910(41)	6.7928
C_V/N	1.7198(19)	1.7163	2.4056(19)	2.3985	1.81571(37)	1.81743
C_p/N	3.929(13)	3.907	4.841(22)	4.808	3.522(8)	3.513
γ_V	0.06058(7)	0.06048	4.981(9)	4.978	1.5052(13)	1.5026
α_p	1.574(8)	1.563	0.4016(28)	0.3977	0.2083(9)	0.2072
β_T	25.98(13)	25.85	0.08064(44)	0.07989	0.1384(6)	0.1379
β_S	11.371(25)	11.354	0.04007(7)	0.03985	0.07134(13)	0.07134
w	1.3045(15)	1.3056	5.5694(48)	5.5835	5.0221(45)	5.0234
μ_{JT}	4.356(35)	4.318	$-0.1557(14)$	-0.1577	$-0.1890(10)$	-0.1914
			$S = k_B \ln \omega$			
N	2922.55(22)		2996.3(1.2)		2871.1(6)	
T	1.19734(17)	1.19734	0.97980(21)	0.97980	3.0245(12)	3.0245
ρ	0.051681(15)	0.051674	0.80463(6)	0.80493	0.55573(13)	0.55546
E/N	1.36071(47)	1.36130	$-4.1095(9)$	-4.1122	1.3925(28)	1.3914
H/N	2.3283(7)	2.3289	$-2.8667(10)$	-2.8699	6.7910(41)	6.7924
C_V/N	1.7194(19)	1.7163	2.4053(19)	2.3985	1.81536(37)	1.81743
C_p/N	3.929(13)	3.907	4.841(22)	4.808	3.522(8)	3.513
γ_V	0.06059(7)	0.06048	4.980(9)	4.978	1.5052(13)	1.5026
α_p	1.574(8)	1.563	0.4017(28)	0.3977	0.2083(10)	0.2072
β_T	25.98(13)	25.85	0.08065(44)	0.07989	0.1384(6)	0.1379
β_S	11.370(25)	11.354	0.04007(7)	0.03985	0.07134(13)	0.07134
w	1.3045(15)	1.3056	5.5693(49)	5.5834	5.0223(45)	5.0234
μ_{JT}	4.357(35)	4.318	$-0.1557(14)$	-0.1577	$-0.1890(18)$	-0.1914

First, we discuss the results of the simulations in the μVL ensemble. In general, for all properties for which Thol *et al.* report uncertainties of the EOS our results agree with the EOS well within its uncertainty. The results for the isochoric heat capacity, isobaric heat capacity, thermal pressure coefficient, and speed of sound exhibit only small deviations between 0.06% and 0.4% from the EOS. The deviations of the isobaric thermal expansivity and isothermal compressibility from the EOS range between -0.008% and $+1\%$, which is well within the uncertainty of the EOS of 15% and 3%. The largest deviation of $+1.5\%$ from the EOS is observed for the Joule–Thomson coefficient at the liquid state, which is also well within the rather high uncertainty of the EOS of 2.5%–10%. At the gas and supercritical states, the deviations of the results for the Joule–Thomson coefficient are much smaller and amount to $+0.5\%$ and $+0.05\%$, respectively. The results for the pressure at the gaseous and supercritical states agree with the EOS within 0.05%, but at the liquid state a deviation of $+0.70\%$ is observed, although the uncertainty of the simulated value is only 0.35%. This rather large deviation

is probably due to the steep rise of the isotherms in the liquid region. We note that Thol *et al.* do not report an uncertainty of the EOS for the pressure, which is usually not done for an empirical equation of state.

In the μpR ensemble, one property less than in the μVL ensemble is calculated because the pressure is prescribed. The uncertainty of the results for the density is somewhat larger than that of the results in the μVL ensemble. It amounts to 0.03% at the gaseous state, 0.0075% at the liquid state, and 0.023% at the supercritical state, while the corresponding uncertainties in the μVL ensemble are 0.0041%, 0.017%, and 0.018%, respectively. This is probably due to the fact that both particle number and volume fluctuate in the μpR ensemble, whereas in the μVL ensemble only the number of particles fluctuates. The results for the density agree with the EOS within 0.05%, which is much less than the uncertainty of the EOS of 0.1%–1.0%.

As in the μVL ensemble, all other properties agree with the EOS well within the uncertainty of the EOS. The results for the isochoric heat capacity, thermal pressure coefficient,

and speed of sound show deviations between -0.025% and $+0.3\%$, while those of the isobaric heat capacity, isobaric thermal expansivity, and isothermal compressibility are somewhat larger and amount to between $+0.1\%$ and $+1.0\%$. Again, the largest deviations from the EOS are observed for the Joule–Thomson coefficient. Here, they lie between $+0.9\%$ and $+1.3\%$. Overall, the very good agreement between the simulation results and the EOS proves that the equations derived in Secs. II and III are correct.

V. CONCLUSIONS

We applied the methodology developed by Lustig for the microcanonical and canonical ensembles to derive expressions for the calculation of thermodynamic properties of fluids in the adiabatic μVL and μpR ensembles in Monte Carlo and molecular-dynamics simulations. Explicit expressions for all common thermodynamic properties and derivatives of the entropy up to third order were obtained by introducing phase-space functions to systematically represent derivatives of the phase-space volume. Equations for phase-space functions of arbitrary order are provided for both ensembles, which allow in principle the calculation of derivatives of the entropy of arbitrary order. The expressions for thermodynamic properties and entropy derivatives were derived for the entropy definitions with the phase-space volume and phase-space density. The equations were explicitly developed for spherical particles, but can readily be adopted for systems of rigid linear or rigid nonlinear molecules as well as mixtures. The equations can also directly be applied in simulations in which quantum corrections are accounted for semiclassically, e.g., by the Feynman-Hibbs corrections because no derivatives with respect to temperature are formed in both ensembles.

The expressions for thermodynamic properties in the μpR ensemble contain terms with the number of particles, the volume, and the potential energy, but no volume derivatives of the potential energy. This is advantageous in simulations with empirical force fields or *ab initio* potential energy surfaces, which are more complex than the simple Lennard-Jones model potential because the computational effort for the calculation of properties such as the isothermal compressibility or speed of sound is smaller than in ensembles in which the volume is an independent variable.

The derived equations were validated by Monte Carlo simulations of the simple Lennard-Jones model fluid at three characteristic state points in both ensembles. The simulation results obtained for all properties agree with the accurate Thol *et al.* EOS for the Lennard-Jones fluid well within the uncertainty of the EOS, which demonstrates that our expressions are correct. The results of these simulations also showed that results for thermodynamic properties obtained with both entropy definitions for large systems agree with each other within their mutual uncertainties. Thus, both entropy definitions can be applied to calculate thermodynamic properties if large systems are simulated.

With the equations for thermodynamic properties derived in this work by the Lustig methodology for the μVL and μpR ensembles, the complete framework for the calculation of thermodynamic properties in the most important seven of the eight basic ensembles of statistical mechanics is available.

We also applied the Lustig methodology to derive expressions for thermodynamic properties in the eighth basic ensemble, the generalized (μpT) ensemble. That work is described in Ref. [54] and will be published in a separate paper.

APPENDIX: ADAPTATION OF THE REFERENCE STATE OF THE EOS TO THE CONVENTIONS OF STATISTICAL MECHANICS

This Appendix describes the adaptation of the reference state of the empirical EOS of Thol *et al.* [50] for the Lennard-Jones model fluid to the conventions of statistical mechanics for the enthalpy and entropy of the ideal gas. In statistical mechanics, the enthalpy per particle of an ideal gas of spherical particles is given by

$$h_{\text{id}} = \frac{5}{2}k_{\text{B}}T, \tag{A1}$$

and the entropy per particle is described by the Sackur-Tetrode equation [40]

$$s_{\text{id}} = k_{\text{B}}\left(\ln\frac{(2\pi m k_{\text{B}})^{3/2}}{h^3} + \frac{5}{2} + \frac{3}{2}\ln T - \ln\rho\right), \tag{A2}$$

where it has been used that the isobaric heat capacity of an ideal gas of spherical particles per particle is $(5/2)k_{\text{B}}$. In phenomenological thermodynamics, however, the enthalpy of the ideal gas is represented by

$$h_{\text{id}} = h_{\text{id}}^0 + \int_{T_0}^{T} c_{p,\text{id}}dT = h_{\text{id}}^0 + \frac{5}{2}k_{\text{B}}(T - T_0), \tag{A3}$$

and the entropy of the ideal gas by

$$s_{\text{id}} = s_{\text{id}}^0 + \int_{T_0}^{T}\frac{c_{p,\text{id}}}{T}\,dT - k_{\text{B}}\ln\frac{\rho T}{\rho_0 T_0}$$
$$= s_{\text{id}}^0 + \frac{3}{2}k_{\text{B}}\ln\frac{T}{T_0} - k_{\text{B}}\ln\frac{\rho}{\rho_0}, \tag{A4}$$

in which T_0 and ρ_0 denote the temperature and density of the reference state and h_{id}^0 and s_{id}^0 are the enthalpy and entropy per particle in the reference state, respectively. If the Thol *et al.* EOS is used to calculate μ, E, H, L, and R, the values of the EOS parameters that fix the values of the enthalpy and entropy to zero in the reference state must be changed such that the enthalpy and entropy of the ideal gas calculated with the EOS agree with Eqs. (A1) and (A2).

The EOS represents the Helmholtz energy of the Lennard-Jones model fluid per particle a as a function of temperature and density. It is formulated in reduced quantities, i.e., in the reduced Helmholtz energy $\alpha = a/k_{\text{B}}T$ as a function of the reduced temperature $\tau = T_{\text{c}}/T$ and the reduced density $\delta = \rho/\rho_{\text{c}}$, where $T_{\text{c}} = 1.32$ and $\rho_{\text{c}} = 0.31$ are the critical temperature and density, respectively. The ideal part of the reduced Helmholtz energy in the EOS has the form

$$\alpha_{\text{id}} = a_1 + a_2\tau + \ln\delta + \frac{3}{2}\ln\tau, \tag{A5}$$

in which a_1 and a_2 are adjustable parameters, whose values were determined such that the enthalpy and entropy of the ideal gas are zero at the reference state. Forming the ideal part

of the reduced Helmholtz energy

$$\alpha_{\text{id}} = \frac{a_{\text{id}}}{k_B T} = \frac{h_{\text{id}}}{k_B T} - 1 - \frac{s_{\text{id}}}{k_B} \tag{A6}$$

by using Eqs. (A3) and (A4) leads to

$$\alpha_{\text{id}} = \left(\frac{h_{\text{id}}^0}{k_B T_c} - \frac{5}{2\tau_0} \right)\tau + \frac{3}{2} - \frac{s_{\text{id}}^0}{k_B} - \frac{3}{2}\ln\tau_0 - \ln\delta_0$$
$$+ \ln\delta + \frac{3}{2}\ln\tau. \tag{A7}$$

Comparing Eq. (A5) to Eq. (A7) yields

$$a_1 = -\frac{s_{\text{id}}^0}{k_B} + \frac{3}{2} - \frac{3}{2}\ln\tau_0 - \ln\delta_0 \tag{A8}$$

and

$$a_2 = \frac{h_{\text{id}}^0}{k_B T_c} - \frac{5}{2\tau_0}. \tag{A9}$$

Agreement of the equations for the ideal gas enthalpy, Eqs. (A1) and (A3), and for the ideal gas entropy, Eqs. (A2) and (A4), requires that

$$h_{\text{id}}^0 = \tfrac{5}{2}k_B T_0 \tag{A10}$$

and

$$s_{\text{id}}^0 = k_B \left(\frac{5}{2} - \ln\rho_0 + \frac{3}{2}\ln\frac{2\pi m k_B T_0}{h^2} \right). \tag{A11}$$

Inserting these results into Eqs. (A8) and (A9),

$$a_1 = \ln\rho_c - \ln\frac{(2\pi m k_B T_c)^{3/2}}{h^3} - 1, \tag{A12}$$

and $a_2 = 0$ is obtained. In the system of dimensionless Lennard-Jones quantities, the Planck constant h, particle mass m, and Boltzmann constant are set to unity. Inserting further the values of the critical temperature and density, yields $a_1 = -5.344446186$. With these choices for a_1 and a_2, values for all thermodynamic properties calculated with the EOS are consistent with those calculated in the Monte Carlo simulations.

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