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Philipp Ströker, Robert Hellmann, and Karsten Meier

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# Systematic Formulation of Thermodynamic Properties in the $NpT$ Ensemble

Philipp Ströker,<sup>\*</sup> Robert Hellmann,<sup>†</sup> and Karsten Meier<sup>‡</sup>

*Institut für Thermodynamik,  
Helmut-Schmidt-Universität / Universität der Bundeswehr Hamburg,  
Holstenhofweg 85, 22043 Hamburg, Germany.*  
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Molecular expressions for thermodynamic properties and derivatives of the Gibbs energy up to third order in the isobaric-isothermal ( $NpT$ ) ensemble 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 Gibbs energy with respect to temperature and pressure. Additionally, expressions for the phase-space functions for temperature-dependent potentials are provided, which, for example, are required when quantum corrections, e.g. Feynman–Hibbs corrections, are applied in classical simulations. The derived expressions are validated by Monte Carlo simulations for the simple Lennard-Jones model fluid at three selected state points. A unique result is that the phase-space functions contain only ensemble averages of combinations of powers of enthalpy and volume. Thus, the calculation of thermodynamic properties in the  $NpT$  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 empirical force fields or very accurate *ab initio* pair and nonadditive three-body potentials.

## I. INTRODUCTION

In statistical mechanics, thermodynamic properties of fluids can be calculated in various ensembles. Each ensemble is characterized by three independent variables, a thermodynamic potential, from which all thermodynamic properties can be obtained as combinations of derivatives of the potential with respect to the independent variables, and a weight factor, with which the systems are distributed in the ensemble. The ensemble theory forms the basis for molecular-dynamics or Monte Carlo simulation techniques [1]. The well-known microcanonical ( $NVE$ ), canonical ( $NVT$ ), and grand canonical ( $\mu VT$ ) ensembles were originally introduced by Gibbs [2]. In 1939, Guggenheim [3] proposed two further ensembles, the isobaric-isothermal ( $NpT$ ) ensemble and the generalized ( $\mu pT$ ) ensemble, in which the chemical potential  $\mu$ , the pressure, and the temperature are independent variables. Later, Byers Brown [4] suggested the  $HpN$  ensemble, Ray *et al.* [5] the  $LV\mu$  ensemble, and Ray and Graben [6] the  $Rp\mu$  ensemble. Graben and Ray [7] summarized the interrelations between these eight ensembles. The microcanonical, canonical, grand canonical, and isothermal-isobaric ensembles are routinely applied in molecular simulations, while the  $HpN$ ,  $LV\mu$ , and  $Rp\mu$  ensembles are rarely used. The generalized ensemble has no applications because the three independent variables are intensive quantities and, thus, the size of the system is indefinite. Moreover, the intensive state of a pure fluid is fixed by two intensive variables, so that the

third variable must be known *a priori* in order to specify it consistently with the other two.

The theory of the microcanonical ensemble, in which the number of particles  $N$ , the volume  $V$ , and the energy  $E$  are independent variables, is well developed. Although it is the starting point for the theoretical formulation of statistical mechanics and forms the natural basis for molecular-dynamics simulations, the exact expressions for the calculation of thermodynamic properties were not known until 1985, when Pearson *et al.* [8] introduced a Laplace transform technique to evaluate the integrals over the momenta of the particles in the microcanonical partition function. This was key for the development of the theory of the microcanonical ensemble. In molecular-dynamics simulations at constant energy, the three components of the total momentum of the particles  $\mathbf{P} = \sum \mathbf{p}_i$ , where  $\mathbf{p}_i$  is the momentum vector of particle  $i$ , are three additional constants of motion. Thus, molecular-dynamics simulations are carried out in a subset of the microcanonical ensemble, the molecular-dynamics ensemble with constant  $NVEP$ . Çağın and Ray [9] used the Laplace-transform technique to extend the treatment of the microcanonical ensemble to the molecular-dynamics ensemble by including the additional constraint of constant total momentum. In a subsequent work, Ray and Zhang [10] recognized that a further quantity  $\mathbf{G} = \mathbf{P}t + \sum m_i \mathbf{r}_i$  which is related to the initial position of the center of mass of the system is also a constant of motion in molecular-dynamics simulations. They once more extended the theory of the molecular-dynamics ensemble to include this additional constraint.

Based on the works of Pearson *et al.* and Ray and co-workers, Lustig [11–15] developed a rigorous methodology to derive expressions for thermodynamic properties, such as the isochoric and isobaric heat capacities,

<sup>\*</sup> philipp.stroeker@hsu-hh.de

<sup>†</sup> robert.hellmann@hsu-hh.de

<sup>‡</sup> karsten.meier@hsu-hh.de

isothermal compressibility, isochoric pressure coefficient, or speed of sound, in the molecular-dynamics and microcanonical ensembles. By introducing so-called phase-space functions to represent derivatives of the partition functions with respect to the independent variables, Lustig derived 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. Recently, Lustig [16, 17] applied the methodology also to the canonical ensemble, in which the number of particles, the volume, and the temperature  $T$  are independent variables, and provided expressions for various thermodynamic properties and derivatives of the Helmholtz energy up to third order. 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.

Until now, expressions for thermodynamic properties in the  $NpT$  ensemble, in which the number of particles  $N$ , the pressure  $p$ , and the temperature  $T$  are independent variables, were derived for only a few thermodynamic properties, and properties related to second-order derivatives of the Gibbs energy are rarely calculated in molecular simulations. Following Guggenheim’s work [3], Hill [18], Byers Brown [4], Münster [19], and Sack [20] elaborated on the theory of the  $NpT$  ensemble. Hill [18] and Byers Brown [4] derived expressions for the volume, enthalpy, isobaric heat capacity, isothermal compressibility, and thermal expansion coefficient. More recently, Lagache *et al.* [21] applied these expressions to calculate isothermal compressibilities, isobaric heat capacities, thermal expansion coefficients, and Joule–Thomson coefficients by Monte Carlo simulations with force field models for  $n$ -alkanes. In this work, we derive explicit expressions for thermodynamic properties and derivatives of the Gibbs energy up to third order in the  $NpT$  ensemble by applying the rigorous methodology developed by Lustig for the microcanonical and canonical ensembles.

This article is organized as follows. The next section provides the theoretical background for the calculation of thermodynamic properties in the  $NpT$  ensemble and presents the general expression for the phase-space functions. The derived equations are validated by Monte Carlo simulations at three state points of the Lennard-Jones model fluid in Sec. III, and Sec. IV presents conclusions.

## II. EXPRESSIONS FOR THERMODYNAMIC PROPERTIES

In the  $NpT$  ensemble, the Gibbs energy  $G$  is the thermodynamic potential, and the number of particles, the pressure, and the temperature are independent variables. As the Helmholtz energy is related to the canonical partition function, the Gibbs energy is related to the partition function  $Z(N, p, \beta)$  of the  $NpT$  ensemble by

$$G = -k_{\text{B}}T \ln Z(N, p, T) = -\beta^{-1} \ln Z(N, p, \beta), \quad (1)$$

where  $k_{\text{B}}$  is the Boltzmann constant and  $\beta = 1/k_{\text{B}}T$  is used as an abbreviation. In the following, it is convenient to use the dimensionless Planck function  $-\beta G = \ln Z$  as thermodynamic potential instead of the Gibbs energy because it reduces applications of the product rule when calculating temperature derivatives.

The partition function of the isothermal-isobaric ensemble was subject to a controversial discussion in the literature. Since the volume of the system is not constant, but fluctuates in the  $NpT$  ensemble, the partition function includes an integration over all volumes accessible to the system, that is, from zero to infinity [3]. This integration introduces the unit of volume into the partition function, which must be compensated for by an appropriately chosen volume scale, so that it is dimensionless. Moreover, for small systems, for instance when studying nucleation phenomena of small droplets or nanoparticles, the volume of the system must be unambiguously defined in order to remove redundant volume states from the partition function. To solve the latter problem, Koper and Reiss [23] introduced a “shell particle,” which is chosen as the particle with the farthest distance from a fixed reference point in the system. The volume of the system is then unambiguously defined by fixing its boundary at the position of the shell particle.

Different proposals for the volume scale were made by Attard [22], Koper and Reiss [23], and Corti and Soto-Campos [24]. Han and Son [25] finally resolved the controversy on the volume scale for small systems. Furthermore, they proved that in simulations of homogeneous systems within periodic boundary conditions the shell particle is not required. If all distances between the particles are fixed in a configuration, identical configurations are generated when the shell particle samples the entire instantaneous volume, since systems in periodic boundary conditions are invariant under translations. Since this work aims at the determination of thermodynamic properties of homogenous macroscopic systems in the thermodynamic limit with simulations performed in periodic boundary conditions, the shell particle is not required here. Han and Son showed that, in this case, the partition function of the  $NpT$  ensemble is given by

$$Z(N, p, T) = N \int_0^{\infty} e^{-\beta pV} Q(N, V, T) V^{-1} dV, \quad (2)$$

where  $Q(N, V, T)$  denotes the canonical partition function and  $N/V$  represents the volume scale. This volume scale was also derived earlier by Attard using information theory [22]. The influence of the volume scale is largest for small systems, but decreases with increasing number of particles and vanishes in the thermodynamic limit ( $N \rightarrow \infty$ ). As will be shown later, it has no influence on the equations for thermodynamic properties, but must be taken into account in the acceptance criterion for volume moves in Monte Carlo simulations.

The following derivation of expressions for thermodynamic properties proceeds in two steps. First, derivatives

of the Planck function with respect to the independent variables and thermodynamic properties are expressed by phase-space functions. Then, equations for the phase-space functions in terms of ensemble averages of combinations of powers of instantaneous values of the volume and enthalpy of the system are derived by comparing derivatives of the partition function with a general equation for an ensemble average in the  $NpT$  ensemble. In the first step, derivatives of the Planck function  $-\beta G$  with respect to  $\beta$  and pressure are expressed in a systematic way through derivatives of the partition function  $Z$  with respect to  $\beta$  and pressure by introducing the abbreviations

$$\mathcal{G}_{mn} = \frac{\partial^{m+n}(-\beta G)}{\partial \beta^m \partial p^n}, \quad m, n = 0, 1, 2, \dots \quad (3)$$

and

$$Z_{mn} = \frac{1}{Z} \frac{\partial^{m+n} Z}{\partial \beta^m \partial p^n}, \quad m, n = 0, 1, 2, \dots \quad (4)$$

In analogy to the phase-space functions of the micro-canonical ensemble  $\Omega_{mn}$  introduced by Lustig, the  $Z_{mn}$  are termed phase-space functions of the  $NpT$  ensemble. Note the special case  $Z_{00} = 1$ . Derivatives of the phase-space function  $Z_{mn}$  with respect to  $\beta$  and pressure can be readily found by using the two recursion formulas

$$\frac{\partial Z_{mn}}{\partial \beta} = Z_{m+1,n} - Z_{10} Z_{mn}, \quad m+n \geq 1, \quad (5)$$

$$\frac{\partial Z_{mn}}{\partial p} = Z_{m,n+1} - Z_{01} Z_{mn}, \quad m+n \geq 1, \quad (6)$$

which can be established by applying the product rule on Eq. (4). Using  $-\beta G = \ln Z$  and Eqs. (4) to (6), the relations presented in Table I for the derivatives of  $-\beta G$  are obtained. The first derivatives with respect to  $\beta$  and  $p$  are found directly by derivation of  $-\beta G = \ln Z$ . From that point onwards, the recursion formulas can be applied to successively calculate the higher derivatives. All relations have the same mathematical structure as the corresponding relations for derivatives of the Massieu function  $-\beta A$  with respect to  $\beta$  and volume in the canonical ensemble [17], with the volume derivatives in the canonical ensemble being replaced by pressure derivatives in the  $NpT$  ensemble.

Next, expressions for the enthalpy and volume in terms of the phase-space functions are derived since they form the basis for the derivation of expressions for further thermodynamic properties and higher derivatives of the Gibbs energy. With the definition of the Gibbs energy  $G = H - TS$ , in which  $H$  is the enthalpy and  $S$  denotes the entropy, and the thermodynamic relation

$$S = - \left( \frac{\partial G}{\partial T} \right)_p = k_B \beta^2 \left( \frac{\partial G}{\partial \beta} \right)_p, \quad (7)$$

the enthalpy

$$H = G + \beta \frac{\partial G}{\partial \beta} = - \frac{\partial(-\beta G)}{\partial \beta} = -Z_{10} \quad (8)$$

TABLE I. Expressions for partial derivatives  $\mathcal{G}_{mn}$  of  $-\beta G$  up to third order in terms of phase-space functions.

$\mathcal{G}_{10} = \frac{\partial(-\beta G)}{\partial \beta} = \frac{\partial \ln Z}{\partial \beta} = \frac{1}{Z} \frac{\partial Z}{\partial \beta} = Z_{10}$
$\mathcal{G}_{20} = Z_{20} - Z_{10}^2$
$\mathcal{G}_{30} = Z_{30} + 2Z_{10}^3 - 3Z_{10}Z_{20}$
$\mathcal{G}_{01} = \frac{\partial(-\beta G)}{\partial p} = \frac{\partial \ln Z}{\partial p} = \frac{1}{Z} \frac{\partial Z}{\partial p} = Z_{01}$
$\mathcal{G}_{02} = Z_{02} - Z_{01}^2$
$\mathcal{G}_{03} = Z_{03} + 2Z_{01}^3 - 3Z_{01}Z_{02}$
$\mathcal{G}_{11} = Z_{11} - Z_{10}Z_{01}$
$\mathcal{G}_{21} = -Z_{01}Z_{20} + Z_{21} + 2Z_{01}Z_{10}^2 - 2Z_{11}Z_{10}$
$\mathcal{G}_{12} = -Z_{10}Z_{02} + Z_{12} + 2Z_{10}Z_{01}^2 - 2Z_{11}Z_{01}$

is expressed by the phase-space function  $Z_{10}$ . Similarly, the volume is related to the phase-space function  $Z_{01}$  by

$$V = \left( \frac{\partial G}{\partial p} \right)_T = -\beta^{-1} \left[ \frac{\partial(-\beta G)}{\partial p} \right]_\beta = -\beta^{-1} Z_{01}. \quad (9)$$

With Eqs. (8) and (9), expressions for further thermodynamic properties can be established. The isobaric heat capacity is given by

$$\begin{aligned} C_p &= \left( \frac{\partial H}{\partial T} \right)_p = -k_B \beta^2 \left[ - \frac{\partial^2(-\beta G)}{\partial \beta^2} \right]_p \\ &= k_B \beta^2 (Z_{20} - Z_{10}^2). \end{aligned} \quad (10)$$

The thermal expansion coefficient is defined as

$$\alpha_p = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_p. \quad (11)$$

Applying Eq. (9) for the volume in Eq. (11) leads to

$$\begin{aligned} \alpha_p &= \frac{k_B \beta^3}{Z_{01}} \left[ \beta^{-2} \frac{\partial(-\beta G)}{\partial p} - \beta^{-1} \frac{\partial^2(-\beta G)}{\partial \beta \partial p} \right] \\ &= \frac{k_B \beta}{Z_{01}} [Z_{01} - \beta (Z_{11} - Z_{10}Z_{01})]. \end{aligned} \quad (12)$$

Analogously, the equation for the isothermal compressibility

$$\beta_T = - \frac{1}{V} \left( \frac{\partial V}{\partial p} \right)_T = - \frac{Z_{02} - Z_{01}^2}{Z_{01}} \quad (13)$$

is obtained. To derive an equation for the isochoric heat capacity

$$C_V = \left( \frac{\partial E}{\partial T} \right)_V = -k_B \beta^2 \left( \frac{\partial E}{\partial \beta} \right)_V, \quad (14)$$

the partial derivative at constant volume must be transformed into derivatives at constant pressure. This transformation is readily performed by the method using Jacobian determinants described by Münster [28, p. 97], which was also applied by Lustig in the canonical ensemble for the derivation of equations for the isobaric heat capacity and other properties [16]. First, the partial derivative is expanded by its invariant property, here  $V$ . Then, both numerator and denominator are differentiated with respect to the independent variables of the

ensemble  $\beta$  and  $p$ , which leads to

$$\begin{aligned} \left( \frac{\partial E}{\partial \beta} \right)_V &\equiv \frac{\partial(E, V)}{\partial(\beta, V)} = \frac{\partial(E, V)}{\partial(\beta, p)} \equiv \frac{\left| \begin{array}{cc} \left( \frac{\partial E}{\partial \beta} \right)_p & \left( \frac{\partial E}{\partial p} \right)_\beta \\ \left( \frac{\partial V}{\partial \beta} \right)_p & \left( \frac{\partial V}{\partial p} \right)_\beta \end{array} \right|}{\left| \begin{array}{cc} \left( \frac{\partial \beta}{\partial \beta} \right)_p & \left( \frac{\partial \beta}{\partial p} \right)_\beta \\ \left( \frac{\partial V}{\partial \beta} \right)_p & \left( \frac{\partial V}{\partial p} \right)_\beta \end{array} \right|} \\ &= \frac{\left( \frac{\partial E}{\partial \beta} \right)_p \left( \frac{\partial V}{\partial p} \right)_\beta - \left( \frac{\partial E}{\partial p} \right)_\beta \left( \frac{\partial V}{\partial \beta} \right)_p}{\left( \frac{\partial V}{\partial p} \right)_\beta}. \end{aligned} \quad (15)$$

The determinant in the denominator simplifies since  $(\partial\beta/\partial p)_\beta = 0$  and  $(\partial\beta/\partial\beta)_p = 1$ . Using additionally  $E = H - pV$  in the numerator yields

$$\left( \frac{\partial E}{\partial \beta} \right)_V = \left( \frac{\partial H}{\partial \beta} \right)_p - \left[ \left( \frac{\partial H}{\partial p} \right)_\beta - V \right] \left( \frac{\partial V}{\partial p} \right)_\beta. \quad (16)$$

Next, the partial derivatives in Eq. (16) are expressed by partial derivatives of the Gibbs energy using Eqs. (8) to (10). Finally, the equation

$$\begin{aligned} C_V &= -k_B \beta^2 \left\{ -\frac{\partial^2(-\beta G)}{\partial \beta^2} - \left[ -\frac{\partial^2(-\beta G)}{\partial p \partial \beta} + \beta^{-1} \frac{\partial(-\beta G)}{\partial p} \right] \frac{\beta^{-2} \frac{\partial(-\beta G)}{\partial p} - \beta^{-1} \frac{\partial^2(-\beta G)}{\partial \beta \partial p}}{-\beta^{-1} \frac{\partial^2(-\beta G)}{\partial p^2}} \right\} \\ &= -k_B \beta^2 \left\{ -(Z_{20} - Z_{10}^2) - \frac{[(-Z_{11} + Z_{10}Z_{01}) + \beta^{-1}Z_{01}][\beta^{-2}Z_{01} - \beta^{-1}(Z_{11} - Z_{10}Z_{01})]}{-\beta^{-1}(Z_{02} - Z_{01}^2)} \right\} \\ &= k_B \left\{ \beta^2 (Z_{20} - Z_{10}^2) - \frac{[Z_{01} - \beta(Z_{11} - Z_{10}Z_{01})]^2}{Z_{02} - Z_{01}^2} \right\} \end{aligned} \quad (17)$$

for the isochoric heat capacity in terms of phase-space functions is obtained.

With the equations for the thermal expansion coefficient, the isothermal compressibility, and the isobaric and isochoric heat capacities, expressions for further thermodynamic properties such as the thermal pressure coefficient  $\gamma_V$ , isentropic compressibility  $\beta_S$ , speed of sound  $w$ , and Joule–Thomson coefficient  $\mu_{JT}$  can be formed. The expressions for all considered thermodynamic properties in terms of phase-space functions are summarized in Table II. In the expression for the speed of sound,  $M$  is the molar mass.

In the second step, the phase-space functions are related to ensemble averages of combinations of the instantaneous values of volume and enthalpy. In this article,

only systems of pure fluids, which consist of spherical particles with three translational degrees of freedom, are considered. 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. The generalization to mixtures is also straightforward and therefore omitted here. For systems of spherical particles, the classical canonical partition function is given by [29]

$$Q(N, V, T) = \frac{1}{N! h^{3N}} \int \int e^{-\beta E} d\mathbf{p}^N d\mathbf{r}^N, \quad (18)$$

TABLE II. Relations for important thermodynamic properties in terms of phase-space functions  $Z_{mn}$ .

isobaric heat capacity	$C_p = \left( \frac{\partial H}{\partial T} \right)_p = k_B \beta^2 (Z_{20} - Z_{10}^2)$
isochoric heat capacity	$C_V = \left( \frac{\partial E}{\partial T} \right)_V = k_B \left\{ \beta^2 (Z_{20} - Z_{10}^2) - \frac{[Z_{01} - \beta(Z_{11} - Z_{10}Z_{01})]^2}{Z_{02} - Z_{01}^2} \right\}$
thermal expansion coefficient	$\alpha_p = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_p = \frac{k_B \beta}{Z_{01}} [Z_{01} - \beta(Z_{11} - Z_{10}Z_{01})]$
isothermal compressibility	$\beta_T = -\frac{1}{V} \left( \frac{\partial V}{\partial p} \right)_T = -\frac{Z_{02} - Z_{01}^2}{Z_{01}}$
thermal pressure coefficient	$\gamma_V = \left( \frac{\partial p}{\partial T} \right)_V = \frac{\alpha_p}{\beta_T} = -k_B \beta \frac{Z_{01} - \beta(Z_{11} - Z_{10}Z_{01})}{Z_{02} - Z_{01}^2}$
isentropic compressibility	$\beta_S = -\frac{1}{V} \left( \frac{\partial V}{\partial p} \right)_S = \beta_T \frac{C_V}{C_p} = -\frac{Z_{02} - Z_{01}^2}{Z_{01}} \left\{ 1 - \frac{[Z_{01} - \beta(Z_{11} - Z_{10}Z_{01})]^2}{\beta^2 (Z_{02} - Z_{01}^2) (Z_{20} - Z_{10}^2)} \right\}$
speed of sound	$w^2 = -\frac{V^2}{NM} \left( \frac{\partial p}{\partial V} \right)_S = \frac{V}{NM \beta_S} = \frac{Z_{01}^2}{NM \beta (Z_{02} - Z_{01}^2) \left\{ 1 - \frac{[Z_{01} - \beta(Z_{11} - Z_{10}Z_{01})]^2}{\beta^2 (Z_{02} - Z_{01}^2) (Z_{20} - Z_{10}^2)} \right\}}$
Joule-Thomson coefficient	$\mu_{JT} = \left( \frac{\partial T}{\partial p} \right)_H = \frac{Z_{11} - Z_{10}Z_{01}}{k_B \beta^2 (Z_{20} - Z_{10}^2)}$

where  $h$  is the Planck constant,  $E$  denotes the energy of the system, and  $d\mathbf{p}^N$  and  $d\mathbf{r}^N$  represent  $3N$ -fold integrations over the momenta and coordinates of the particles. Insertion of Eq. (18) into Eq. (2) yields the expression

$$Z(N, p, T) = \frac{N}{N! h^{3N}} \int_0^\infty \int \int e^{-\beta(E+pV)} V^{-1} d\mathbf{p}^N d\mathbf{r}^N dV \quad (19)$$

for the partition function of the  $NpT$  ensemble. Thus, in the  $NpT$  ensemble, systems are distributed according to the distribution

$$\exp[-\beta(E + pV)] V^{-1} = \exp(-\beta H) V^{-1}.$$

When the potential energy depends only on the coordinates of the particles, the energy of the system is split into the kinetic energy  $K = \sum \mathbf{p}_i^2/2m_i$  and the potential energy  $U$ . The integrals over the momenta can then be evaluated as in the canonical ensemble, so that

$$Z(N, p, T) = C \int_0^\infty \int \beta^{-3N/2} e^{-\beta(U+pV)} V^{-1} d\mathbf{r}^N dV \quad (20)$$

is obtained, where the abbreviation

$$C = \frac{N (2\pi m)^{3N/2}}{N! h^{3N}} \quad (21)$$

has been introduced. The ensemble average of an arbitrary property  $A$  in the  $NpT$  ensemble, denoted as  $\langle A \rangle$ ,

is given by

$$\langle A \rangle = \frac{C \int \int A \beta^{-3N/2} e^{-\beta(U+pV)} V^{-1} d\mathbf{r}^N dV}{C \int \int \beta^{-3N/2} e^{-\beta(U+pV)} V^{-1} d\mathbf{r}^N dV}. \quad (22)$$

Since the constant  $C$  cancels and does not affect derivatives with respect to pressure and temperature, it is omitted in the following, whereas the term  $\beta^{-3N/2}$  must be retained because it plays an important role in the derivation of expressions for derivatives with respect to temperature.

Expressions for the phase-space functions  $Z_{mn}$  are found by differentiating Eq. (20) with respect to  $\beta$  and  $p$  and comparing the result with the integrand in the numerator in Eq. (22) to identify the expression corresponding to the property  $A$ . Since the enthalpy depends linearly on pressure, the derivatives with respect to  $p$  are readily obtained. For example, the phase-space function  $Z_{01}$  is found as

$$Z_{01} = \frac{\int \int \beta^{-3N/2} (-\beta V) e^{-\beta(U+pV)} V^{-1} d\mathbf{r}^N dV}{\int \int \beta^{-3N/2} e^{-\beta(U+pV)} V^{-1} d\mathbf{r}^N dV}, \quad (23)$$

in which the numerator on the right hand side is the derivative of the partition function with respect to pressure, and the denominator corresponds to the partition function in the term  $1/Z$  in the definition of the phase-space function. Comparing Eq. (23) with Eq. (22) yields

$$Z_{01} = -\beta \langle V \rangle. \quad (24)$$

This comparison also reveals that the volume scale has no influence on the expressions for the phase-space functions because the term  $V^{-1}$  appears in both equations in the integrands in the numerators.

Similarly, the phase-space function  $Z_{10}$  (the first derivative of the partition function with respect to  $\beta$ ) follows as

$$\begin{aligned} Z_{10} &= \frac{\int \int -\frac{3N}{2} \beta^{-3N/2-1} e^{-\beta(U+pV)} V^{-1} \mathbf{dr}^N dV}{\int \int \beta^{-3N/2} e^{-\beta(U+pV)} V^{-1} \mathbf{dr}^N dV} \\ &+ \frac{\int \int \beta^{-3N/2} (-U - pV) e^{-\beta(U+pV)} V^{-1} \mathbf{dr}^N dV}{\int \int \beta^{-3N/2} e^{-\beta(U+pV)} V^{-1} \mathbf{dr}^N dV} \\ &= -\frac{3N}{2} \beta^{-1} - \langle U + pV \rangle = -\frac{3N}{2} \beta^{-1} - \langle \hat{H} \rangle. \end{aligned} \quad (25)$$

The quantity  $\hat{H} = U + pV$  is the sum of the potential energy and the product of pressure and volume. It was termed configurational enthalpy by Lagache *et al.* [21]. The kinetic energy is explicitly shown by the first term in the last line of Eq. (25), whereas the pressure in the configurational enthalpy contains kinetic and potential contributions. Expressions for phase-space functions with higher and mixed derivatives can be derived accordingly. The expressions for phase-space functions up to third order are listed in Table III.

It is a remarkable result that the expressions for the phase-space functions do not contain volume derivatives of the potential energy as in the microcanonical and canonical ensembles. Here, only averages of combinations of the volume and configurational enthalpy appear, which can be calculated with little computational effort in a Monte Carlo simulation.

By mathematical induction, the general representation for the phase-space functions

$$Z_{mn} = \left( \frac{3N/2}{-\beta} \right)^m \sum_{j=0}^m \binom{m}{j} \mathcal{P}_{-n, m-j}^{3N/2} \left\langle \left( \frac{\beta \hat{H}}{3N/2} \right)^j (-\beta V)^n \right\rangle \quad (26)$$

can be obtained. The symbol  $\mathcal{P}_{x',x}^X$  denotes the Pochhammer polynomials [30] defined by Lustig as [17]

$$\mathcal{P}_{x',x}^X = \begin{cases} 1, & \text{for } x = 0 \text{ or } (x' = 0 \text{ and } x = 1), \\ \left( 1 + \frac{x'}{X} \right) \left( 1 + \frac{x'+1}{X} \right) \dots \left( 1 + \frac{x'+x-1}{X} \right), & \\ \text{otherwise.} & \end{cases} \quad (27)$$

They describe the terms arising from the derivatives of the term  $\beta^{-3N/2}$  in the partition function with respect to  $\beta$ .

Inserting the expressions from Table III for the classical phase-space functions into the relations for the thermodynamic properties in Table II yields the following equations for the thermodynamic properties in terms of ensemble averages of combinations of the volume and configurational enthalpy:

$$C_p = \frac{3}{2} N k_B + \frac{1}{k_B T^2} \left( \langle \hat{H}^2 \rangle - \langle \hat{H} \rangle^2 \right), \quad (28)$$

$$\begin{aligned} C_V &= \frac{3}{2} N k_B + \frac{1}{k_B T^2} \left( \langle \hat{H}^2 \rangle - \langle \hat{H} \rangle^2 \right) \\ &- \frac{1}{k_B T^2} \frac{\left( \langle \hat{H} V \rangle - \langle \hat{H} \rangle \langle V \rangle \right)^2}{\langle V^2 \rangle - \langle V \rangle^2}, \end{aligned} \quad (29)$$

$$\alpha_p = \frac{1}{k_B T^2} \frac{\langle \hat{H} V \rangle - \langle \hat{H} \rangle \langle V \rangle}{\langle V \rangle}, \quad (30)$$

$$\beta_T = \frac{1}{k_B T} \frac{\langle V^2 \rangle - \langle V \rangle^2}{\langle V \rangle}, \quad (31)$$

$$\gamma_V = \frac{1}{T} \frac{\langle \hat{H} V \rangle - \langle \hat{H} \rangle \langle V \rangle}{\langle V^2 \rangle - \langle V \rangle^2}. \quad (32)$$

These equations agree with those reported by Hill [18] and Byers Brown [4]. Thus, the rigorous methodology of Lustig yields the same expressions for thermodynamic properties in the  $NpT$  ensemble as those derived by the standard theory of fluctuations [18]. The equations for the isentropic compressibility, speed of sound, and third-order derivatives of the Gibbs energy in Tables I to III, to the best of our knowledge, have not yet been reported in the literature. In principle, equations for derivatives of the Gibbs energy of arbitrary order can be derived by using the recursion formulas, Eqs. (5) and (6), and the general equation for the phase-space functions, Eq. (26).

Finally, we discuss the extension of the formalism to temperature-dependent potentials (TDP). In molecular simulations with accurate *ab initio* potential energy surfaces of real fluids, quantum effects are often taken into account semi-classically by applying temperature-dependent corrections such as the Feynman-Hibbs quantum corrections [32]. When calculating temperature derivatives, the dependence of the potential on temperature must be taken into account. For example, the extended expression for the phase-space function corresponding to the first temperature derivative of the partition function reads

$$Z_{10}^{\text{TDP}} = -\frac{3N}{2} \beta^{-1} - \left\langle U(\beta) + \beta \frac{\partial U(\beta)}{\partial \beta} + pV \right\rangle. \quad (33)$$

Expressions for phase-space functions for temperature-dependent potentials up to third order are also reported in Table III. They have the same mathematical structure as the corresponding expressions for the canonical ensemble [31]. The expressions are generally valid for any temperature-dependent potential. For the lowest-order Feynman–Hibbs quantum corrections, the derivatives of the potential with respect to  $\beta$  of second and higher orders vanish. In contrast, the classical expressions for phase-space functions corresponding to pure pressure derivatives remain unchanged for temperature-dependent potentials.

### III. VALIDATION BY MONTE CARLO SIMULATIONS OF A MODEL FLUID

To validate the expressions derived in Sec. II, Monte Carlo simulations of the simple Lennard-Jones model fluid at three state points were performed in the  $NpT$  ensemble with the Metropolis algorithm [33] as described by Allen and Tildesley [1]. The original Metropolis Monte Carlo algorithm for the canonical ensemble was first extended to the  $NpT$  ensemble by Wood for simulations of hard disks [34, 35] and subsequently by McDonald [36, 37] for simulations of particles interacting by continuous potentials. A Fortran 90 program was developed from the code F.12 provided as supplement with the book of Allen and Tildesley [1]. Since a different volume scale in the partition function was used by Allen and Tildesley, the acceptance criterion for volume moves had to be modified in order to include the volume scale  $N/V$  applied in Eq. (2). Thus, the Metropolis scheme was implemented to generate a Markov chain whose limiting distribution is proportional to

$$\exp[-\beta\hat{H} + (N-1)\ln V],$$

which contains the term  $N-1$  instead of  $N$  in the original code of Allen and Tildesley. Thus, volume moves were accepted with the probability

$$\min\{1, \exp[-\beta\Delta\hat{H}_{nm} + (N-1)\ln(V_n/V_m)]\},$$

where  $\Delta\hat{H}_{nm}$  denotes the difference of the configurational enthalpy between states  $n$  and  $m$  of the Markov chain and  $V_n$  and  $V_m$  are the volumes of the system in the  $n$ th and  $m$ th state of the Markov chain.

Throughout this section, the usual Lennard-Jones dimensionless quantity system is used, in which all thermodynamic properties are reduced by the length parameter  $\sigma$  and well depth  $\varepsilon$  of the Lennard-Jones potential. All symbols used in this section represent dimensionless quantities. The state points ( $T = 1.2$ ,  $p = 0.05$ ) in the gas region, ( $T = 1.0$ ,  $p = 1.0$ ) in the liquid region, and ( $T = 3.0$ ,  $p = 9.0$ ) in the supercritical region were simulated. With this choice, three characteristic states in the fluid region are investigated. Since we are interested in thermodynamic properties of macroscopic systems in

the thermodynamic limit, simulations were carried out with 108, 256, 500, 864, and 1372 particles at each state point, and the results for all properties were extrapolated to the thermodynamic limit  $N \rightarrow \infty$ . All simulations were started from a cubic-face-centered lattice configuration. After an equilibration phase of  $10^5$  cycles, each simulation comprised  $10^7$  cycles with  $N-1$  particle moves and one volume move per cycle. The cutoff radius was always set to half of the box length, and the long-range correction for the potential energy to account for interactions between pairs of particles whose distance is larger than the cutoff radius was calculated as described by Allen and Tildesley [1]. Both cutoff radius and long-range correction were adapted when the volume was changed. During the production phase of the simulation, instantaneous values for all ensemble averages required in the expressions for the phase-space integrals in Table III were accumulated at the end of each cycle. After the production phase had been completed, ensemble averages, and with them the phase-space functions, were calculated. Values for the thermodynamic properties were then obtained by using the relations in Table II. The uncertainties of the simulation results were estimated by means of the method of statistical inefficiency as recommended by Allen and Tildesley [1], which is originally due to Friedberg and Cameron [38]. For the uncertainty analysis, instantaneous values of thermodynamic properties, which are combinations of several ensemble averages, were estimated by the method proposed by Lustig [11].

The extrapolation of the results to the thermodynamic limit was carried out with a second-order polynomial fit to the data for density and enthalpy as a function of the inverse number of particles at the liquid and supercritical states because these data have very low uncertainties and could not be represented within their uncertainty by a linear fit. For the density and enthalpy at the gaseous state and all other properties, a linear fit was used. The results for the thermodynamic limit and their uncertainties (at the 0.95 confidence level) are reported in Table IV. Included in the table are values calculated with the reference equation of state (EOS) by Thol *et al.* [39], which has been shown by Stephan *et al.* [40] to be among the most accurate representations of the properties of the Lennard-Jones model fluid. According to Thol *et al.* [39], the uncertainties of their EOS amount to 0.1% in density, 0.5% in isochoric heat capacity, 1% in isobaric heat capacity and speed of sound, 2.5% to 10% in the Joule–Thomson coefficient, 15% in the thermal expansion coefficient, 3% in isothermal compressibility, and 1% in the thermal pressure coefficient.

Results for selected properties are shown in Fig. 1 as a function of the inverse number of particles. All extrapolated simulation results agree with the equation of state well within its uncertainty. The agreement is best for density and enthalpy, while the other properties that are determined by combinations of second-order derivatives of the Gibbs energy show somewhat larger deviations.



TABLE III. Explicit expressions for phase-space functions  $Z_{mn}$  up to third order for ordinary and temperature-dependent potentials in the  $NpT$  ensemble.

$$Z_{10} = -\frac{3N}{2}\beta^{-1} - \langle \hat{H} \rangle$$

$$Z_{20} = \frac{3N}{2} \left( \frac{3N}{2} + 1 \right) \beta^{-2} + 3N\beta^{-1} \langle \hat{H} \rangle + \langle \hat{H}^2 \rangle$$

$$Z_{30} = -\frac{3N}{2} \left( \frac{3N}{2} + 1 \right) \left( \frac{3N}{2} + 2 \right) \beta^{-3} - \frac{9N}{2} \left( \frac{3N}{2} + 1 \right) \beta^{-2} \langle \hat{H} \rangle - \frac{9N}{2} \beta^{-1} \langle \hat{H}^2 \rangle - \langle \hat{H}^3 \rangle$$

$$Z_{01} = -\beta \langle V \rangle$$

$$Z_{02} = \beta^2 \langle V^2 \rangle$$

$$Z_{03} = -\beta^3 \langle V^3 \rangle$$

$$Z_{11} = \left( \frac{3N}{2} - 1 \right) \langle V \rangle + \beta \langle \hat{H}V \rangle$$

$$Z_{21} = -\frac{3N}{2} \left( \frac{3N}{2} - 1 \right) \beta^{-1} \langle V \rangle - 2 \left( \frac{3N}{2} - 1 \right) \langle \hat{H}V \rangle - \beta \langle \hat{H}^2V \rangle$$

$$Z_{12} = -\left( \frac{3N}{2} - 2 \right) \beta \langle V^2 \rangle - \beta^2 \langle \hat{H}V^2 \rangle$$

$$Z_{10}^{\text{TDP}} = -\frac{3N}{2}\beta^{-1} - \left\langle U(\beta) + \beta \frac{\partial U(\beta)}{\partial \beta} + pV \right\rangle$$

$$Z_{20}^{\text{TDP}} = \frac{3N}{2} \left( \frac{3N}{2} + 1 \right) \beta^{-2} + 3N\beta^{-1} \left\langle U(\beta) + \beta \frac{\partial U(\beta)}{\partial \beta} + pV \right\rangle + \left\langle \left( U(\beta) + \beta \frac{\partial U(\beta)}{\partial \beta} + pV \right)^2 \right\rangle - \left\langle 2 \frac{\partial U(\beta)}{\partial \beta} + \beta \frac{\partial^2 U(\beta)}{\partial \beta^2} \right\rangle$$

$$\begin{aligned} Z_{30}^{\text{TDP}} = & -\frac{3N}{2} \left( \frac{3N}{2} + 1 \right) \left( \frac{3N}{2} + 2 \right) \beta^{-3} - \frac{9N}{2} \left( \frac{3N}{2} + 1 \right) \beta^{-2} \left\langle U(\beta) + \beta \frac{\partial U(\beta)}{\partial \beta} + pV \right\rangle \\ & - \frac{9N}{2} \beta^{-1} \left\langle \left( U(\beta) + \beta \frac{\partial U(\beta)}{\partial \beta} + pV \right)^2 \right\rangle + \frac{9N}{2} \beta^{-1} \left\langle 2 \frac{\partial U(\beta)}{\partial \beta} + \beta \frac{\partial^2 U(\beta)}{\partial \beta^2} \right\rangle - \left\langle \left( U(\beta) + \beta \frac{\partial U(\beta)}{\partial \beta} + pV \right)^3 \right\rangle \\ & + 3 \left\langle \left( U(\beta) + \beta \frac{\partial U(\beta)}{\partial \beta} + pV \right) \left( 2 \frac{\partial U(\beta)}{\partial \beta} + \beta \frac{\partial^2 U(\beta)}{\partial \beta^2} \right) \right\rangle - \left\langle 3 \frac{\partial^2 U(\beta)}{\partial \beta^2} + \beta \frac{\partial^3 U(\beta)}{\partial \beta^3} \right\rangle \end{aligned}$$

$$Z_{11}^{\text{TDP}} = \left( \frac{3N}{2} - 1 \right) \langle V \rangle + \beta \left\langle \left( U(\beta) + \beta \frac{\partial U(\beta)}{\partial \beta} + pV \right) V \right\rangle$$

$$\begin{aligned} Z_{21}^{\text{TDP}} = & -\frac{3N}{2} \left( \frac{3N}{2} - 1 \right) \beta^{-1} \langle V \rangle - 2 \left( \frac{3N}{2} - 1 \right) \left\langle \left( U(\beta) + \beta \frac{\partial U(\beta)}{\partial \beta} + pV \right) V \right\rangle - \beta \left\langle \left( U(\beta) + \beta \frac{\partial U(\beta)}{\partial \beta} + pV \right)^2 V \right\rangle \\ & + \beta \left\langle \left( 2 \frac{\partial U(\beta)}{\partial \beta} + \beta \frac{\partial^2 U(\beta)}{\partial \beta^2} \right) V \right\rangle \end{aligned}$$

$$Z_{12}^{\text{TDP}} = -\left( \frac{3N}{2} - 2 \right) \beta \langle V^2 \rangle - \beta^2 \left\langle \left( U(\beta) + \beta \frac{\partial U(\beta)}{\partial \beta} + pV \right) V^2 \right\rangle$$

The data for density and enthalpy have the lowest uncertainties of all calculated properties and agree with the EOS within 0.04% and 0.07%, respectively. The isochoric heat capacities and speeds of sound also show small deviations of up to 0.2% from the EOS, while the data for the Joule–Thomson coefficient exhibit the largest deviations

from the EOS with up to 0.65% at the liquid state, for which the uncertainty of the EOS is also large. The deviations of the other properties from the EOS range from 0.2% to 0.5%. The very good agreement between the simulation results and the EOS confirms the correctness of the equations derived in Sec. II.

TABLE IV. 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.* [39] for several thermodynamic properties at three state points of the Lennard-Jones model fluid. Each simulation comprised  $10^7$  cycles. The simulations were carried out with 108, 256, 500, 864, and 1372 particles. The values reported are extrapolated values in the thermodynamic limit  $N \rightarrow \infty$ . Expanded uncertainties are given by the numbers in parentheses, i.e., 4.323(17) means that the value 4.323 has an expanded uncertainty of 0.017.

property	gas		liquid		supercritical	
	$T = 1.2, p = 0.05$		$T = 1.0, p = 1.0$		$T = 3.0, p = 9.0$	
	simulation	EOS	simulation	EOS	simulation	EOS
$\rho$	0.051476(14)	0.051461	0.79878(48)	0.79847	0.80270(16)	0.80275
$H/N$	2.3382(7)	2.3393	-2.775(6)	-2.773	11.6169(43)	11.6175
$C_p/N$	3.9074(11)	3.8889	4.79(7)	4.80	3.468(9)	3.471
$C_V/N$	1.7171(24)	1.7136	2.379(5)	2.376	2.1285(22)	2.1288
$\alpha_p$	1.5580(23)	1.5505	0.399(8)	0.401	0.10465(5)	0.10489
$\beta_T$	25.83(7)	25.77	0.0828(9)	0.0829	0.0306(9)	0.0306
$\gamma_V$	0.06031(7)	0.06017	4.815(40)	4.833	3.4233(45)	3.4234
$\beta_S$	11.352(25)	11.355	0.041185(7)	0.041027	0.018765(23)	0.018793
$w$	1.3080(14)	1.3082	5.5159(24)	5.5251	8.148(5)	8.142
$\mu_{JT}$	4.323(17)	4.300	-0.1573(43)	-0.1563	-0.2465(11)	-0.2460

#### IV. CONCLUSIONS

Using the systematic methodology developed by Lustig for the microcanonical and canonical ensembles, equations have been derived that can be used in Monte Carlo simulations in the  $NpT$  ensemble to calculate macroscopic thermodynamic properties of fluids. By introducing phase-space functions to represent derivatives of the partition function, explicit expressions for all common thermodynamic properties and derivatives of the Gibbs energy up to third order have been obtained. In principle, expressions for derivatives of the Gibbs energy up to arbitrary order can be derived with the methodology. Furthermore, expressions for temperature-dependent potential models are provided, which are required when quantum corrections are taken into account. The expressions for third-order derivatives of the Gibbs energy and for temperature-dependent potentials are reported here for the first time. All derived expressions are applicable for spherical particles, rigid linear molecules, and rigid non-linear molecules as well as mixtures. The derived equations were validated by Monte Carlo simulations of the

simple Lennard-Jones model fluid at three characteristic state points.

Compared to the canonical and microcanonical ensembles, our expressions for thermodynamic properties contain only ensemble averages of combinations of the volume and enthalpy of the system, but no volume derivatives of the potential energy. This is advantageous for simulations with empirical force fields or *ab initio* potential energy surfaces for real molecules, which are much more complex than the simple Lennard-Jones model potential. Without the need to compute volume derivatives of the potential energy, the computational effort for the calculation of properties such as the isothermal compressibility and the speed of sound in the  $NpT$  ensemble is smaller than in ensembles in which the volume is an independent variable.

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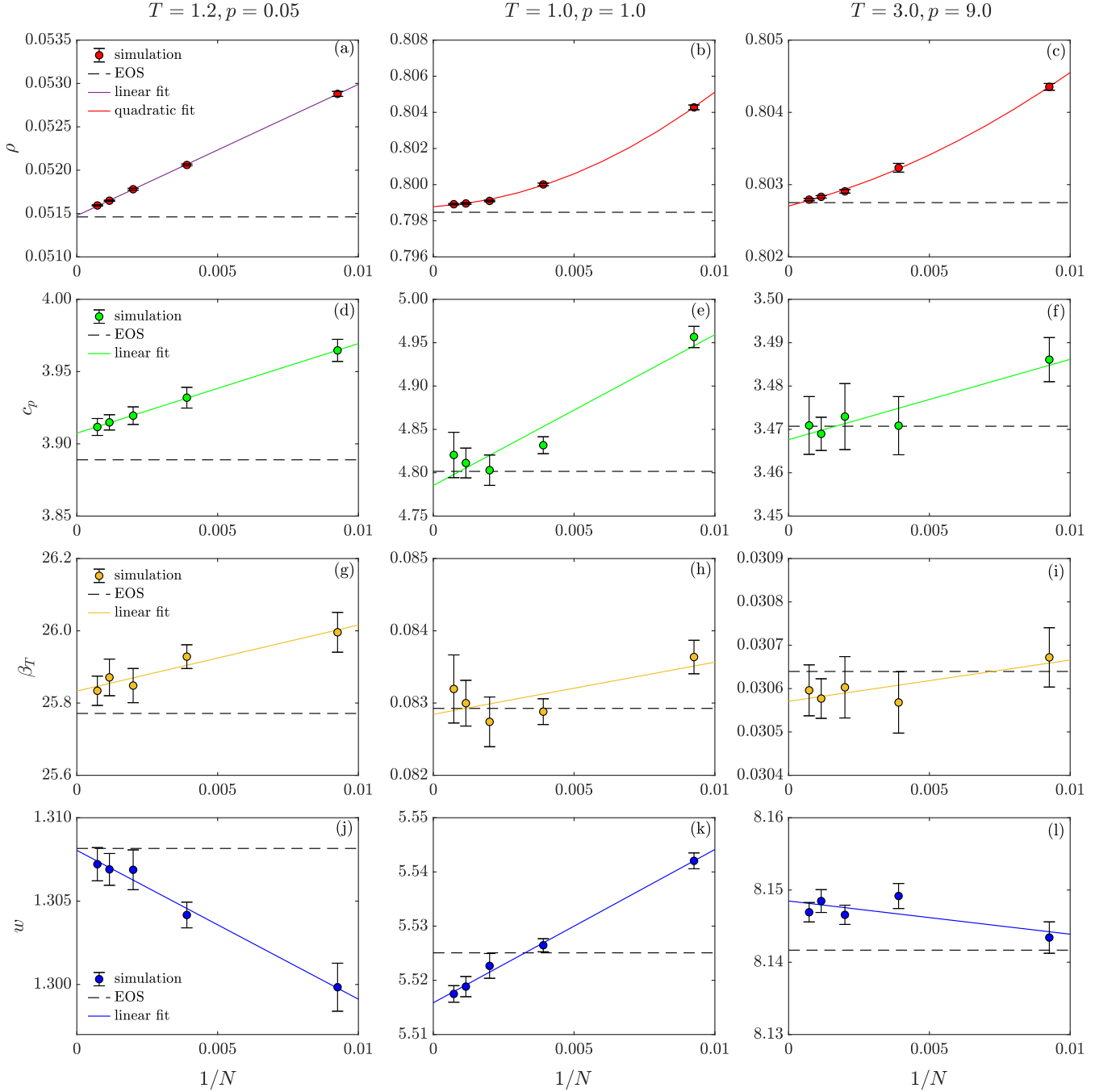


FIG. 1. Results of the Monte Carlo simulations for selected thermodynamic properties at three state points of the Lennard-Jones model fluid as a function of the inverse number of particles (panels a–l). The error bars show expanded uncertainties (at the 0.95 confidence level) of the simulation results, and the dashed lines represent values calculated with the EOS of Thol *et al.* [39].

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