Prediction of sound velocity in normal alkanes: A configurational-bias Monte Carlo simulation approach

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ABSTRACT

We propose a Monte Carlo computational approach to obtain the velocity of sound in fluids, based on the fluctuation method [F.A. Escobedo, J. Chem. Phys. 108 (1998) 8761]. The technique involves a sequential implementation of the isobaric-isothermal and canonical ensembles in a simulation box, in which the (residual) thermodynamic derivative properties are evaluated via the fluctuation method during configurational-bias Monte Carlo simulation. We specifically tested our Monte Carlo theory to compute the velocity of sound in a number of (linear) alkane fluids (methane, n-butane, n-heptane, and n-decane). In the case of methane, we employed a united atom Lennard-Jones potential [D. Möller, J. Oprzynski, A. Möller, J. Fischer, Mol. Phys. 75 (1992) 363]. We present an analysis of the bulk pair correlation function for methane near its critical temperature, which potentially reveals structural differences to explain the extrema phenomena in heat capacities as well as sound velocity differences at such corresponding extrema states. In the case of n-butane, n-heptane, and n-decane, we used an optimized anisotropic united atom intermolecular Lennard-Jones description of Ungerer et al. [P. Ungerer, C. Beauvais, J. Delhommelle, A. Boutin, B. Rousseau, A.H. Fuchs, J. Chem. Phys. 112 (2000) 5499] along with the intramolecular parameters of Nieto-Draghi and Ungerer [C. Nieto-Draghi, P. Ungerer, J. Chem. Phys. 125 (2006) 044517]. We provided extensive comparison with the experimental data in the temperature range between 273.15 and 432.15 K and pressures up to 50 MPa. In excellent agreement with the experiment, we find the Monte Carlo technique to be capable of predicting the velocity of sound in the fluids studied in the present analysis, with improved accuracy in higher pressures at which the validity of the fluctuation theory has been established.

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1. Introduction

In general, the characteristics of fluid responses to sound waves (i.e. sound velocities) are indicators of the state and structure of the fluid, and can subsequently be related to other properties of the fluid through thermodynamic concepts [1]. Hence, the sound velocity information in fluids shall be of great value in many aspects. For instance, the information of sound velocity has been of extensive use in the petroleum exploration and production to determine the hydrocarbon saturation in reservoir rocks [2], and to monitor the reservoir conditions during the Enhanced Oil Recovery process [3,4]. Successful reports have been quoted in the literature on utilizing the sound velocity for modeling purposes [5–9], and on accurate prediction of thermodynamic properties in fluids through estimation of virial coefficients [10] using the sound velocity data, all of which attest to the potential usefulness of the sound velocity information in fluids.

From a thermodynamic perspective, the velocity of sound is related to second-order derivates of thermodynamic potentials (Gibbs energy, Helmoltz energy, enthalpy, and internal energy). Such determination of the second-order differentials is of major difficulty in thermodynamics, owing to deficiency of the available equations of state in accurate prediction of second-order derivative quantities, albeit their fairly good ability in estimation of properties of the first-order derivative group (i.e. phase equilibria calculations) [11].

The literature contains previous reports [12,13] on prediction of sound velocity in fluids, which share the common approach of applying a thermodynamic equation of state for this purpose. Some authors [13], for example, have shifted to an essentially more complicated equation of state, based upon the statistical associating fluid theory (SAFT-BACK) [13–15] to improve accuracy.

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We offer an alternative route for prediction of sound velocity by Monte Carlo simulation, which allows computations to be made over a wide range of temperature and pressure. The evaluation of sound velocity by our approach will entail simultaneous determination of other thermodynamic second-order derivative quantities (i.e. thermal expansivity, isothermal compressibility, heat capacity) for the conditions involved. Quantitative prediction of such second-order derivative properties is attainable by performing Monte Carlo simulations at various temperatures or pressures [16] during numerous runs, or alternatively by applying the statistical fluctuation theory [17] to analyze the results obtained within a single simulation run.

We will employ the statistical fluctuation theory [17] for our analysis, which enables to keep the required computational time for our Monte Carlo simulations within a reasonable length. The fluctuation theory states the derivative of a property X with respect to an intensive variable Y to be related to the fluctuations of $\langle XZ \rangle - \langle X \rangle \langle Z \rangle$ in the considered statistical ensemble, in which Z is the conjugate extensive variable of Y [18]. We will utilize the mentioned technique to obtain computational estimates for the isothermal compressibility and thermal expansivity, which are derivative properties with respect to pressure and temperature, respectively. Nevertheless, the numerical evaluation of heat capacity shall require a more elegant approach. As a matter of fact, the kinetic part of energy, which contributes to the value of heat capacities, cannot be computed via the two simulation ensembles considered herein. For this sake, the recommended approach [18] suggests the heat capacity being evaluated as the sum of a residual heat capacity and an ideal heat capacity, which are obtained from the Monte Carlo simulation and the experimental correlations, respectively.

A section will follow, in which we will mention and essentially derive some basic equations involved in the present work. A third section is devoted to an explanation of our simulation method, in which we shall mention the intermolecular as well as intramolecular parameters employed for molecular simulations in the present analysis.

A fourth section is dedicated to mention our Monte Carlo simulation results, ensued by our concluding remarks.

2. Theoretical background

In thermodynamics, the basic relationship to compute the sound velocity (c) in a fluid, relates this quantity to the (bulk) compressibility at constant entropy (β_s) by [20]

$$c^2 = \frac{\upsilon}{M\beta_s} \tag{1}$$

where

$$\beta_s = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_S \tag{2}$$

where υ is the molar volume, and M is the molar mass of the fluid. With only few exemptions [20], Eq. (1) yields nearly identical results for sound velocities as to the experimental values for most fluids, thus should be a reliable basis for numerical estimation of this quantity. Applying the fundamental thermodynamic relationships, Eq. (1) can be written in an equivalent form in terms of the isothermal compressibility (β_T) as

$$c^2(T, P) = \frac{C_p(T, P)}{C_v(T, \langle V \rangle)} \frac{\upsilon(T, P)}{M\beta_T(T, P)} \tag{3}$$

where C_p and C_v are the molar heat capacities at constant pressure and constant volume, respectively. Indeed, Eq. (3) will serve as the basis for our computational analysis in the present work. Hence, it should be evident that computation of sound velocity by Monte Carlo simulation in this approach will entail simultaneous

determination of the heat capacities and the isothermal compressibility, which are obtainable by analyzing the fluctuations in the simulation results in their corresponding statistical ensembles as described below.

In the following, we shall initially define the partition function for a single-component system in an isobaric-isothermal ensemble, based on which we will derive the fluctuation formula to obtain the thermal expansivity. Basically, a similar approach will be applicable to extract the fluctuation formulas for calculation of isothermal compressibility and residual heat capacity during an isobaric-isothermal (NPT) Monte Carlo simulation. The approach should equally be legitimate to obtain the fluctuation formula for the residual heat capacity under the canonical (NVT) ensemble, or to be further extended to derive such fluctuation relationships in multi-component systems in either ensemble.

The partition function for a single-component system composed of N (rigid) molecules in an isobaric-isothermal (NPT) ensemble reads [21]

$$\Delta = \int \frac{V^N}{N!\,\Lambda^{3N}} \, \exp(-\beta\hat{H}) \, dV \, d\zeta^n \tag{4}$$

with Λ being the de Broglie wavelength of the molecule, V being the volume of the system, ζ being the dimensionless degrees of freedom, n being the number of degrees of freedom, and $\hat{H}$ being the configurational enthalpy defined as

$$\hat{H} = U^{ext} + U^{int} + PV \tag{5}$$

in which, U^{ext} and U^{int} represent the intermolecular and intramolecular potential energies, respectively. Accordingly, the ensemble average of a property X can be evaluated via:

$$\langle X \rangle = \frac{1}{\Delta} \int \frac{XV^N}{N!\,\Lambda^{3N}} \, \exp(-\beta\hat{H}) \, dV \, d\zeta^n \tag{6}$$

Since the derivatives of the de Broglie wavelength with respect to temperature cancel out [18], one may establish the following equality:

$$\left(\frac{\partial\langle X \rangle_{NPT}}{\partial\beta}\right)_P = \langle X \rangle_{NPT}\langle\hat{H}\rangle_{NPT} - \langle X\hat{H}\rangle_{NPT} \tag{7}$$

where $\beta = 1/kT$, with k being the Boltzmann constant and T being the temperature of the system. Here, the subscript to the brackets refers to the simulation ensemble under which the average properties are recorded.

Consequently, the expression to compute the thermal expansivity (α_P) is obtained as [18]

$$\alpha_P = \frac{1}{\langle V \rangle_{NPT}kT^2}(\langle V\hat{H}\rangle_{NPT} - \langle V \rangle_{NPT}\langle\hat{H}\rangle_{NPT}) \tag{8}$$

Similarly, the equation for the isothermal compressibility can be derived as [18]

$$\beta_T = \frac{1}{\langle V \rangle_{NPT}kT}(\langle V^2 \rangle_{NPT} - \langle V \rangle_{NPT}^2) \tag{9}$$

For heat capacity, the derivation will follow a somewhat different route. Indeed, solely analyzing the fluctuations in the Monte Carlo simulation results may be insufficient by itself to yield correct predictions for heat capacity, since the kinetic energy contribution to this quantity will be neglected through the two simulation ensembles considered herein. As mentioned earlier, the recommended approach [19] suggests addition of an ideal heat capacity term to the residual heat capacity value obtained via Monte Carlo simulation. The former is responsible for inclusion of the kinetic