Efficient pressure estimation in molecular simulations without evaluating the virial

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I. INTRODUCTION

Estimation of the pressure in molecular simulations is usually accomplished via calculation of the virial. However, for complex intermolecular potential functions, calculation of the virial can be computationally expensive. Computational expense often dictates infrequent evaluation of the virial during a simulation, which in turn leads to high statistical uncertainties in pressure. Special attention has been paid to developing efficient techniques for estimating the virial for systems of polyatomic fluids.

Eppenga and Frenkel presented a method for estimation of pressure which does not require the evaluation of the virial and is based on a numerical calculation of the derivative of the free energy with respect to volume. They applied the method to a system of hard platelets. The method has received scant attention since its proposal. In the present work we generalize the Eppenga and Frenkel method to potentials which involve attractive forces and to calculation of pressure in the Gibbs ensemble. We validate the method by calculating the vapor pressure of the Lennard-Jones fluid and models for carbon dioxide, and methanol.

II. DERIVATION AND RESULTS

Following Eppenga and Frenkel, we seek to evaluate pressure in the canonical ensemble using the derivative of Helmholtz free energy with respect to volume. Calculation of the pressure can be achieved by performing “test” or “virtual” volume moves, exactly similar to insertion of “ghost” particles or removing of real particles when evaluating the chemical potential by Widom insertions.

The partition function $Q$ for the canonical ensemble is given by

$$Q = \int_{V} \frac{V^{N}}{\Lambda^{N} N!} \exp(-\beta U) d\tau,$$

where $\Lambda$ is the de Broglie wavelength, $U$ is the energy of the system, and $\beta = 1/k_{B}T$. The integration is performed over all possible configurations of the system in coordinates scaled with the box length.

We can calculate pressure by estimating the derivative of the Helmholtz free energy with respect to volume

$$P = \left. \frac{dA}{dV} \right|_{N,T} = \frac{-\Delta A}{\Delta V} = +k_{B}T \frac{1}{\Delta V} \ln \frac{Q_{V'}}{Q_{V}},$$

where the difference in free energy ($\Delta A$) is calculated for a volume change of $\Delta V = V' - V$, from $V$ to $V'$.

We have that

$$\frac{Q_{V'}}{Q_{V}} = \int_{V} \frac{V'^{N}}{\Lambda^{N} N!} \exp(-\beta U_{V'}) d\tau$$

$$= \left\{ \left( \frac{V'}{V} \right)^{N} \exp(-\beta \Delta U) \right\},$$

where $\Delta U = U_{V'} - U_{V}$ and $\langle \cdots \rangle$ is the ensemble average in the canonical ensemble.

Consequently,

$$P = \frac{k_{B}T}{\Delta V} \ln \left\{ \left( \frac{V'}{V} \right)^{N} \exp(-\beta \Delta U) \right\}.$$

The above expression is accurate as long as $\Delta V$ is small and the derivative $dA/dV$ in Eq. (2) is correctly approximated. $\Delta V$ should be constant (in both magnitude and sign) while the ensemble average in Eq. (4) is being evaluated. Thus the ratio $V'/V$ is constant for the canonical ensemble and, for $V'/V$ close to unity, Eq. (4) becomes

$$P = \frac{k_{B}T}{V} + \frac{1}{\Delta V} \ln \langle \exp(-\beta \Delta U) \rangle.$$

Equation (5) has been presented and used by Eppenga and Frenkel, with the restriction that only volume reductions are allowed for hard core systems. Smit and Frenkel have presented a generalization of Widom’s test particle expression to the Gibbs ensemble. In a way precisely analogous to the Smit and Frenkel derivation in Ref. 10, it can be shown that Eq. (4) is valid for the Gibbs ensemble. In this case, $V$ and $N$ represent the fluctuating volume and the number of molecules of the phase for which we want to evaluate the pressure.

Equation (4) is meaningful only in the case of the constant-volume Gibbs ensemble, in which the total system volume does not fluctuate. For mixtures, on the other hand, one can perform constant-pressure Gibbs simulations. In this case, use of Eq. (4) would not provide an independent test on the validity of the simulation, in contrast to a virial-route pressure calculation, and should not be utilized.
For monoatomic fluids interacting with potentials which scale simply with volume (such as Lennard-Jones or Stockmayer potentials) calculation of the virial or of energy change due to a (virtual) volume change can be achieved at almost zero computational cost.\(^1\) However, for polyatomic fluids, calculating the virial or attempting volume changes is computationally expensive. In this respect, the proposed method for calculating the pressure is expected to have significant advantages over the conventional virial method, only for ensembles in which the volume must fluctuate, as is the case for the Gibbs ensemble.

Volume steps are usually performed by picking a volume change in the interval \((-\Delta V_{\text{max}}, +\Delta V_{\text{max}})\), where \(\Delta V_{\text{max}}\) is adjusted during the course of the simulation so that the trial volume moves are accepted with a target acceptance ratio. The proposed method demands that \(|\Delta V|\) remains constant while the ensemble average is evaluated. This does not pose any problem if \(\Delta V/V\) is relatively small. The use of a uniform step for volume changes has the added advantage that no computational time is wasted on small volume moves which have a high probability of acceptance, but do not move the system quickly through configuration space.

In order to validate our method, a series of Gibbs ensemble simulations have been performed. First, we examined the effect of \(|\Delta V|\) in the calculation of pressure for the Lennard-Jones fluid at \(T^* = k_B T/\varepsilon\) equal to 1.25, 1.00, and 0.75. Both positive and negative values of \(\Delta V\) were used, with identical results within the statistical uncertainties. Selected results are shown in Table I and compared with literature values.\(^{11}\) The pressure of the liquid phase has a much larger statistical uncertainty than that of the vapor phase, as is the case when the virial method is used. Reasonably good statistics for the pressure of the liquid phase are obtained when \(|\Delta V|/V_{\text{liquid}}\) is less than about 2%.

Finally, we calculated the vapor pressure of polyatomic fluids interacting with Lennard-Jones plus coulombic potentials, namely methanol\(^8\) and carbon dioxide.\(^7\) Our simulation results are compared with the previous results in Table II. Only the pressure of the gas phase is shown, but the pressure of the liquid was equal to the pressure of the gas within its (larger) statistical uncertainty. Excellent agreement with the literature simulation data is obtained for all fluids and temperatures examined.

### ACKNOWLEDGMENTS

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\(^{a}\)Reference 8.  
\(^{b}\)Reference 7.

### Table I. Results for the pure Lennard-Jones fluid.

<table>
<thead>
<tr>
<th>(T^*)</th>
<th>(1000 \delta V/(V_0))</th>
<th>(\rho_\pm)</th>
<th>(\rho_\mp)</th>
<th>(P_\pm)</th>
<th>(P_\mp)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.75</td>
<td>0.313</td>
<td>0.823 (4)</td>
<td>0.0037 (4)</td>
<td>-0.007 (19)</td>
<td>0.0027 (3)</td>
</tr>
<tr>
<td>1.56</td>
<td>0.821 (5)</td>
<td>0.0036 (6)</td>
<td>0.001 (60)</td>
<td>0.0026 (4)</td>
<td></td>
</tr>
<tr>
<td>Virial method</td>
<td>0.824 (6)</td>
<td>0.0041 (4)</td>
<td>0.010 (1)</td>
<td>0.0030 (3)</td>
<td></td>
</tr>
<tr>
<td>Loth et al.(^{a})</td>
<td>0.821 58(38)</td>
<td>0.003 93(10)</td>
<td>0.002 64 (7)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.00</td>
<td>0.547</td>
<td>0.704 (4)</td>
<td>0.031 (2)</td>
<td>0.027 (11)</td>
<td>0.0255(08)</td>
</tr>
<tr>
<td>2.72</td>
<td>0.702 (3)</td>
<td>0.030 (2)</td>
<td>0.007 (15)</td>
<td>0.0258(10)</td>
<td></td>
</tr>
<tr>
<td>Virial method</td>
<td>0.701 (10)</td>
<td>0.029 (3)</td>
<td>0.034 (25)</td>
<td>0.0248(25)</td>
<td></td>
</tr>
<tr>
<td>Loth et al.(^{a})</td>
<td>0.700 81(38)</td>
<td>0.029 64(32)</td>
<td>0.025 05(22)</td>
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<tr>
<td>1.25</td>
<td>0.465</td>
<td>0.523 (07)</td>
<td>0.132 (10)</td>
<td>0.102 (7)</td>
<td>0.095 (2)</td>
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<tr>
<td>2.16</td>
<td>0.501 (19)</td>
<td>0.129 (11)</td>
<td>0.096 (5)</td>
<td>0.096 (2)</td>
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<tr>
<td>Virial method</td>
<td>0.519 (15)</td>
<td>0.134 (23)</td>
<td>0.096 (3)</td>
<td>0.098 (7)</td>
<td></td>
</tr>
<tr>
<td>Loth et al.(^{a})</td>
<td>0.512 5 (26)</td>
<td>0.133 0 (67)</td>
<td>0.097 3 (11)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^{a}\)Reference 11.