Molecular Dynamics Calculation of the Thermodynamic Properties of Methane

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Abstract

Thermodynamic properties of methane in the dense gas and liquid states have been calculated by the method of molecular dynamics. The methane pair interactions were modelled using a spherically symmetric $m$–6–8 potential, and the most significant three-body and quantum effects were included. Agreement between calculated and experimental values for the energy and pressure is generally good except at low temperatures and high densities. The specific heat at constant volume is also briefly discussed.

Introduction

Recently we have calculated the self-diffusion coefficient of dense gas and liquid methane using the method of molecular dynamics (Hanley and Watts 1975). The principal objective of that study was to investigate how well a simple spherically symmetric model pair potential, with parameters determined solely from the bulk properties of the dilute gas, represented transport properties of the liquid at moderate and high densities. The $m$–6–8 potential of Hanley and Klein (1972) (also Klein and Hanley 1972) was selected as the model. Agreement between calculated and experimental coefficients was generally good, suggesting that it would be worth while to study other properties of the dense fluid. In this paper we report the thermodynamic properties of methane corresponding to the self-diffusion coefficients in the previous study, again modelling the methane intermolecular interactions by the spherically symmetric $m$–6–8 potential. Specifically, results for the pressure and energy at six densities, and (to a somewhat lesser extent) the specific heat at constant volume at five densities, are compared with comprehensive experimental measurements carried out at the National Bureau of Standards (Goodwin 1971, 1974). We will show that agreement between calculations and experiment is generally satisfactory thus strengthening the conclusion from our previous study that the $m$–6–8 is a good effective pair potential for methane in the dense gas and liquid states.

The $m$–6–8 potential has the form

$$\phi^*(r^*) = \frac{6+2\gamma}{m-6}\left(\frac{d}{r^*}\right)^m - \frac{m - \gamma(m-8)}{m-6}\left(\frac{d}{r^*}\right)^6 - \gamma\left(\frac{d}{r^*}\right)^8,$$  \hspace{1cm} (1)$$

where $\phi^* = \phi/\epsilon$, with $\epsilon$ the well depth; $d = r_{\text{min}}/\sigma$ and $r^* = r/\sigma$, with $\phi(r_{\text{min}}) = -\epsilon$ and $\phi(\sigma) = 0$; and $m$ and $\gamma$ are parameters respectively determining the strengths of the repulsive term and of the attraction due to an $r^{-8}$ contribution. Parameters
for equation (1) that are appropriate to methane were obtained from dilute gas data by the procedure discussed in detail by Hanley and Klein (1972); the values taken were:

\[ m = 11, \gamma = 3 \cdot 0, \sigma = 3 \cdot 680 \times 10^{-10} \text{m} (r_{\text{min}} = 4 \cdot 101 \times 10^{-10} \text{m}), \varepsilon/k = 168 \cdot 0 \text{K}. \]

These parameters were used without adjustment in our previous study of the self-diffusion coefficient, and they are used again here.

**Computer Simulation**

The molecular dynamics calculations were based on the general techniques developed by several authors for a microcanonical ensemble (Verlet 1967, and references therein) and followed in particular the method discussed by Barker et al. (1971) for argon. Consequently no more than a very brief description is given here.

A given number \( N (= 108 \) in our work) of particles were placed in a cubic box and the standard periodic boundary conditions were imposed to approximate an infinite system. For computational convenience the potential energy of the system was assumed to be pairwise additive, so that we defined an energy \( U_{0}^{*} \) by the relation

\[ U_{0}^{*} = \sum_{i \neq j}^{N} \phi_{ij}^{*}, \]

where \( \phi_{ij}^{*} = \phi^{*}(|r_{ij}^{*} - r_{ij}^{*}|) = \phi^{*}(r^{*}) \), and in addition the potential was truncated at a distance \( r = 2 \cdot 5 \sigma \). Corrections for the truncation together with terms including quantum and three-body effects are considered below. The equations of motion of the system,

\[ \frac{d^{2}r_{i}^{*}}{dt^{2}} = -\sum_{i \neq j}^{N} \frac{d\phi_{ij}^{*}}{dr_{ij}^{*}}, \]

were solved numerically using a finite difference algorithm for several values of the reduced number density \( \rho^{*} = (N/V)\sigma^{3} \) and reduced temperature \( T^{*} = kT/e \) (here \( k \) is Boltzmann’s constant, \( V \) the volume and \( T \) the temperature). We obtained values for the positions \( r_{i}^{*} \) and velocities \( v_{i}^{*} \) of the particles as a function of successive time steps \( \delta t^{*} \). The reduced time is given by the relation \( t^{*} = t(e/m)^{3}\sigma^{-1} \), where \( m \) is the molecular mass, and \( \delta t^{*} \) was set equal to 0.008018, corresponding to a real time of \( 10^{-14} \) s. Having established that the system was in equilibrium (Fisher 1971), we recorded the positions and velocities of the particles for about 5400 time steps and the thermodynamic properties of the system were obtained using appropriate time averages (Verlet 1967). Thus, for the reduced internal energy \( E^{*} \) one has

\[ E^{*} = \langle U_{0}^{*} \rangle = \langle \sum_{i \neq j}^{N} \phi_{ij}^{*} \rangle \]

and for the equation of state

\[ pV/NkT = 1 + (NT^{*})^{-1} \langle P_{0} \rangle, \]

where

\[ P_{0} = -\frac{1}{3} \sum_{i \neq j}^{N} r^{*} \frac{d\phi_{ij}^{*}}{dr}, \quad r^{*} \leq 2 \cdot 5. \]
If it is assumed that the pair distribution function has reached its asymptotic form at the distance \( r^* = 2.5 \), a straightforward correction compensates for the truncation of the potential. One adds terms to \( E^* \) and \( pV/NkT \) given by

\[
E^*_\infty = 2\pi N\rho^* \int_{2.5}^{\infty} \phi_{ij} r^{*2} dr^*
\]

and

\[
(pV/NkT)_\infty = -\frac{3}{2}\pi \rho^*(T^*)^{-1} \int_{2.5}^{\infty} (d\phi_{ij}/dr^*) r^{*3} dr^* .
\]

Barker and his co-workers have discussed in detail the importance of many-body forces in the liquid state (Barker et al. 1971, 1972, 1974). Their work has shown, in particular, that one cannot obtain an accurate representation of experimental thermodynamic data from computer simulation methods using a realistic pair potential together with equations (5)–(9). Since preliminary molecular dynamics studies with the \( m-6-8 \) potential for argon (Janssone and Verbeke 1972; W. R. Streett, personal communication) are consistent with this conclusion, one would expect therefore that many-body forces would have to be included in the calculations of the thermodynamic properties of methane discussed here. Accordingly, following Barker et al. (1971) we write for the potential energy

\[
U^* = \sum_{i<j}^N \phi_{ij} + \sum_{i<j<k}^N \phi_{ijk}
\]

or

\[
U^* = U^*_6 + U^*_8,
\]

where \( U^*_6 \) is the sum over all pair interactions in the system as before and \( U^*_8 \) is a three-body potential. We further assume that the three-body intermolecular interactions are represented by the Axilrod–Teller triple dipole expression

\[
\phi_{123} = v(1 + 3 \cos \theta_1 \cos \theta_2 \cos \theta_3)/s_1^3 s_2^3 s_3^3,
\]

in which \( s_1, s_2, s_3 \) and \( \theta_1, \theta_2, \theta_3 \) are the sides and interior angles of the triangle formed by the centres of the three molecules. The coefficient \( v \) in the Axilrod–Teller equation is given approximately as \( v = \frac{3}{4} \alpha C_6 \), where \( \alpha \) is the polarizability of the methane molecule and \( C_6 \) the coefficient of the inverse sixth-power term of potential (1). Since

\[
C_6 = \{m - \gamma(m-8)\} d^6 e^6 e/(m-6)
\]

and \( \alpha \) has been determined experimentally as \( 2.59 \times 10^{-30} \text{ m}^3 \) (Straty and Goodwin 1973), we have that \( v = 85.74 \times 10^{-109} \text{ J m}^9 \). Barker et al. (1972, 1974) have given convincing arguments that equation (11) adequately represents many-body forces in the liquid and solid states of the noble gases. As many of the properties of the methane molecule resemble those of the noble gas atoms, we assume without further discussion that the Axilrod–Teller potential is the dominant many-body interaction in methane.

Three-body forces can be introduced into the calculation using perturbation theory. In principle, since the molecular dynamics method models a microcanonical ensemble, the perturbation expansion should be carried out in this ensemble. However,
in the thermodynamic limit, properties such as the internal energy are independent of the ensemble in which they are calculated. In addition, Lebowitz et al. (1967) have shown that, for intensive variables depending only upon the temperature and space coordinates, the differences between fluctuations measured in the canonical and microcanonical ensembles are proportional to the specific heat. Consequently it is convenient to calculate the contributions from three-body interactions by perturbation theory in the canonical ensemble (Zwanzig 1954).

From perturbation theory it is found that one obtains, to first order in \( v \) (Barker et al. 1971)

\[
A = kT \ln \left( \left(1^{-3N}/N! \right) Z_o \right) + \langle U_3 \rangle, \tag{12}
\]

where \( \lambda = (h^2/2\pi mkT)^\frac{1}{2} \) and \( Z_o \) is the configurational integral for the two-body classical system:

\[
Z_o = \int \cdots \int \exp \{-\beta U_0\} \, dr_1 \cdots dr_N, \tag{13}
\]

where \( \beta = 1/kT \). The angle bracket notation indicates a weighted average of the form

\[
\langle X \rangle = Z_o^{-1} \int \cdots \int \exp \{-\beta U_0\} X \, dr_1 \cdots dr_N.
\]

Note that the average is with respect to a system whose particles interact through the truncated pair potential and whose total internal energy is defined by equation (3).

Perturbation theory is a powerful and flexible tool to use in the analysis of the computer results. For example, we can easily extend the above procedure to include quantum corrections, as was done in the argon work. Using the Wigner-Kirkwood expansion of the free energy in powers of \( h^2 \) (Landau and Lifshitz 1958) and expanding the free energy to first order in \( v \) and \( h^2 \), one obtains a term additional to that given in equation (12), so that

\[
A = kT \ln \left( \left(1^{-3N}/N! \right) Z_o \right) + \langle U_3 \rangle + \frac{\beta h^2}{96\pi^2 m} \left( \sum_{i<j} \nabla_i^2 \phi_{ij} \right), \tag{14}
\]

where \( \nabla_i^2 \) is the Laplacian operator at \( r_i \).

Differentiation of equation (14) with respect to temperature gives the expression for the thermodynamic internal energy used in this work, before correction for the truncation of the potential:

\[
E^* = \langle U_0^* \rangle + \langle U_3^* \rangle - (T^*)^{-1} \{ \langle U_3^* U_0^* \rangle - \langle U_3^* \rangle \langle U_0^* \rangle \} + 2 \langle U_3^* \rangle

- (T^*)^{-1} \{ \langle U_3^* U_0^* \rangle - \langle U_3^* \rangle \langle U_0^* \rangle \}. \tag{15}
\]

In this expression we have, from equation (10),

\[
U_3^* = \sum_{i<j<k} \phi_{ijk}^*,
\]

and

\[
U_3^* = \frac{h^2(\sigma^2 e T^*)^{-1}}{96\pi^2 m} \sum_{i<j} \sum \frac{d^2 \phi_{ij}^*}{dr_i^2}. \tag{16}
\]
Table 1. Calculated contributions to total energy and pressure, and comparison with experiment
Note that at \( p = 440.9 \) and 347.4 kg m\(^{-3}\), \( E_\infty \) and \( p_\infty \) were calculated from equations (21) and (22) respectively

(a) Total energy \( E_T \)

<table>
<thead>
<tr>
<th>( \rho ) (kg m(^{-3}))</th>
<th>( T ) (K)</th>
<th>Contributions to ( E_T ) (kJ mol(^{-1}))</th>
<th>( E_T ) Exp. (kJ mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>440.9</td>
<td>121.5</td>
<td>(-6.831 -0.214 0.074 0.168 12.206)</td>
<td>5.403  4.641</td>
</tr>
<tr>
<td>151.4</td>
<td>(-6.577 -0.215 0.065 0.168 12.960)</td>
<td>6.402  5.625</td>
<td></td>
</tr>
<tr>
<td>347.4</td>
<td>172.7</td>
<td>(-5.083 -0.169 0.036 0.095 13.498)</td>
<td>8.376  7.697</td>
</tr>
<tr>
<td>220.0</td>
<td>(-4.854 -0.170 0.032 0.091 14.696)</td>
<td>9.794  9.135</td>
<td></td>
</tr>
<tr>
<td>258.7</td>
<td>202.8</td>
<td>(-3.695 -0.129 0.023 0.056 14.257)</td>
<td>10.51  9.931</td>
</tr>
<tr>
<td>224.8</td>
<td>(-3.598 -0.129 0.020 0.053 14.817)</td>
<td>11.16  10.59</td>
<td></td>
</tr>
<tr>
<td>192.4</td>
<td>196.7</td>
<td>(-2.821 -0.096 0.018 0.040 14.103)</td>
<td>11.24  10.64</td>
</tr>
<tr>
<td>213.0</td>
<td>(-2.743 -0.096 0.017 0.039 14.517)</td>
<td>11.73  11.18</td>
<td></td>
</tr>
<tr>
<td>171.0</td>
<td>205.9</td>
<td>(-2.507 -0.085 0.015 0.028 14.315)</td>
<td>11.78  11.25</td>
</tr>
<tr>
<td>133.6</td>
<td>204.7</td>
<td>(-1.988 -0.067 0.013 0.022 14.316)</td>
<td>12.28  11.77</td>
</tr>
<tr>
<td>233.0</td>
<td>(-1.897 -0.067 0.010 0.020 14.967)</td>
<td>13.03  12.67</td>
<td></td>
</tr>
</tbody>
</table>

(b) Pressure \( p \)

<table>
<thead>
<tr>
<th>( \rho ) (kg m(^{-3}))</th>
<th>( T ) (K)</th>
<th>Contributions to ( p ) (MPa)</th>
<th>( p ) Exp. (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>440.9</td>
<td>121.5</td>
<td>(-12.89 4.57 12.28)</td>
<td>37.68  39.93</td>
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<tr>
<td>151.4</td>
<td>(-12.94 3.98 12.59)</td>
<td>86.84  91.76</td>
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</tr>
<tr>
<td>347.4</td>
<td>172.8</td>
<td>(-8.25 1.77 4.62)</td>
<td>23.07  17.44</td>
</tr>
<tr>
<td>220.0</td>
<td>(-8.32 1.33 4.93)</td>
<td>56.36  49.81</td>
<td></td>
</tr>
<tr>
<td>258.7</td>
<td>202.8</td>
<td>(-4.75 0.38 1.10)</td>
<td>13.41  10.12</td>
</tr>
<tr>
<td>224.8</td>
<td>(-4.75 0.34 1.39)</td>
<td>22.74  17.81</td>
<td></td>
</tr>
<tr>
<td>192.4</td>
<td>196.7</td>
<td>(-2.62 0.13 0.45)</td>
<td>8.64  5.74</td>
</tr>
<tr>
<td>213.0</td>
<td>(-2.62 0.13 0.42)</td>
<td>11.78  8.85</td>
<td></td>
</tr>
<tr>
<td>171.0</td>
<td>205.9</td>
<td>(-2.08 0.04 0.27)</td>
<td>9.23  7.02</td>
</tr>
<tr>
<td>133.6</td>
<td>204.7</td>
<td>(-1.27 0.11 0.25)</td>
<td>7.80  6.24</td>
</tr>
<tr>
<td>233.0</td>
<td>(-1.27 0.06 0.24)</td>
<td>11.33  9.49</td>
<td></td>
</tr>
</tbody>
</table>

Differentiation of the free energy with respect to the volume gives (Born and Green 1947) the corresponding expression for the pressure \( p \), written here in terms of the compressibility factor:

\[
pV/NkT = 1+(NT*)^{-1}\{\langle P_0 \rangle + \langle P_3 \rangle + \langle PQ \rangle\}
\]

\[
-(NT*)^{-2}\{\langle U_3^* P_0 \rangle - \langle U_3^* \rangle \langle P_0 \rangle + \langle U_3^* \rangle \langle P_0 \rangle - \langle U_3^* \rangle \langle P_0 \rangle\}, \tag{17}
\]

where

\[
P_Q = -\frac{1}{N} \sum_{i<j} r^* dU_3^*/dr^*
\]

and

\[
P_3 = 3U_3^*, \tag{19}
\]

the last result following from Euler's theorem on homogeneous functions (Barker et al. 1971).
Results and Discussion

Total Energy and Pressure

For each thermodynamic state the two-body contributions to the energy and pressure were obtained from a time average using every fifth time step. The three-body and quantum corrections were evaluated after every fiftieth time step and averaged accordingly. The results of the calculations are shown in Tables 1a and 1b, in which the total energy $E_T$ and the pressure $p$ have been tabulated for the various temperatures and mass densities $\rho$. Experimental data for these properties are also included for comparison. The subscripts on the column headings have the following interpretations: $2\cdot5$, results from the two-body molecular dynamics calculation with the truncated potential; $\infty$, from corrections due to the truncation; $Q$, from the quantum correction; $3b$, from the three-body Axilrod–Teller corrections. $E^0$ is the energy of the isolated molecule, including intramolecular vibrational and rotational contributions, extracted from an independent calculation (Tester 1961; Goodwin 1974).

We note first from Table 1 the relative magnitudes of the various contributions to the energy and pressure. It is seen that the quantum and three-body corrections to the energy are small and thus justify using a perturbation expansion of the free energy to facilitate their calculation. However, as was observed by Barker et al. (1971) for argon, the effect of these corrections on the pressure is often substantial. Note, especially, the magnitude of the three-body correction terms. The long-range two-body corrections are of the order of $4-5\%$ for the energy and are definitely significant in the computation of the pressure. For this reason, we verified that the corrections given by equations (8) and (9) are sufficient using the following argument.

An energy $U^*_2$ was defined as the sum of the pairwise molecular interactions for a potential acting over the interval $2\cdot5 < r^* \leq 1\cdot5 L/\sigma$, where $L = V^4$, $V$ being the volume of the cubic box in the molecular dynamics calculation. The total energy becomes, therefore,

$$U^* = U^*_0 + U^*_{3b} + U^*_2,$$

(20)

where $U^*_0$ and $U^*_3$ are defined by equations (10) and (10a), and

$$U^*_2 = \sum_{i<j} \phi_i^j(r^*) \quad \text{for} \quad 2\cdot5 < r^* \leq 1\cdot5 L/\sigma.$$

Equation (20) was included in the equation for the free energy and the perturbation expansion was carried out as previously described, but now including terms of first order in $\beta U_2$. Alternative expressions for $E^*_\infty$ and $(pV/NkT)_\infty$ result:

$$E^*_\infty = \langle U^*_2 \rangle - (T^*)^{-1}\{\langle U^*_0 U^*_2 \rangle - \langle U^*_0 \rangle \langle U^*_2 \rangle \}$$

(21)

and

$$(pV/NkT)_\infty = (NT^*)^{-1}\langle P_2 \rangle - (NT^*)^{-1}\{\langle U^*_2 P_0 \rangle - \langle U^*_2 \rangle \langle P_0 \rangle \},$$

(22)

where

$$P_2 = -\frac{1}{2} \sum_{i<j} r^* d\phi_i^j/dr^*, \quad 2\cdot5 < r^* \leq 1\cdot5 L/\sigma.$$

(23)

To these equations we must add contributions from (8) and (9) respectively with the qualification that the lower limit of the $r^*$ integrations becomes $1\cdot5 L/\sigma$. The agreement between energies calculated using equations (8) and (21), and between compress-
Molecular Dynamics Calculations for Methane

The statistical errors on our machine results can be estimated by comparing corresponding pressures and energies averaged over varying numbers of configurations for a given equilibrium state. We assigned an error of about ±1 MPa in the pressures and about ±0.05 kJ mol⁻¹ in the energies from such comparisons. A further estimate of the statistical errors can be obtained by referring to the calculation of Barker et al. (1971) for liquid argon. In that work, equivalent results from molecular dynamics and Monte Carlo calculations were compared: values of the pressure differed by about 0.1–1 MPa and values of the energy by less than 0.05 to about 0.5 kJ mol⁻¹, depending on the thermodynamic state of the fluid. We would expect similar differences for methane. The approximation of the infinite system by a periodic system of 108 particles can also be expected to introduce errors, and this possibility is discussed with reference to the specific heat in the last part of this section. Overall, a reasonable estimate of the precision of our molecular dynamics results is ±5 MPa in the pressure and ±0.3 kJ mol⁻¹ in the energy.

The experimental pressures and energies listed in Table 1 are taken from a very comprehensive experimental program used to determine accurately the thermodynamic properties of methane. Data for pVT were measured over a wide range of experimental conditions (Goodwin and Prydz 1971) and coordinated with independent measurements of the melting and vapour pressures (Prydz and Goodwin 1972), dielectric constant (Straty and Goodwin 1973), refractive index (J. D. Olson, personal communication), specific heat (Younglove 1974) and the speed of sound (Van Dael et al. 1965; Van Itterbeek et al. 1967; Straty 1974). Based on these diverse data, an equation of state was proposed by Goodwin (1974). The interpolated experimental data given in this paper were obtained from a computer analysis of these data (McCarty 1974). An approximate error of ±0.5 MPa has been given to the experimental pressures and ±0.02 kJ mol⁻¹ to the energy. These errors will be somewhat larger at very high densities and close to the critical density.

Inspection of Table 1 shows that our calculated values tend to be somewhat higher than experiment. Nevertheless, the agreement between these values and experiment is considered satisfactory. It should be stressed at this point that the discrepancies can be reduced substantially if the parameters σ and ε/k are very slightly adjusted. Barker et al. (1971) emphasized the sensitivity of the pressure of the dense fluid to these scaling parameters when they proposed their accurate pair potential for argon. However, we did not pursue this approach, primarily because the parameters used here are firmly based on a correlation of the properties of dilute gaseous methane (Klein and Hanley 1972; Hanley and Watts 1975) and we do not wish to disrupt this agreement. In any case, the basic assumption used in this study of methane, namely the neglect of nonspherical effects, is such that revised values for σ and ε/k would probably have no real significance. It is also worth recalling that the motivation for this work was to establish how effectively an approximate and simple pair potential determined from bulk properties of the dilute gas can be used at higher densities. We believe that this objective has been achieved for the internal energy and equation of state.
Specific Heat at Constant Volume

The comparison of our results with experiment is concluded with a discussion of results for the specific heat at constant volume, \( C_v \). The comparison is interesting because it illustrates very well some of the problems associated with the computer simulation of a real liquid.

\[ C_v = (C_v - C_v^0) = \frac{\partial \langle U \rangle}{\partial T}, \]

(24)

where \( C_v \) is the total specific heat and \( C_v^0 \) is the ideal gas value. Let us consider the methane system, but neglect quantum and three-body forces. Given then that \( U^* = U_0^* + U_\text{int}^* \), one can derive the expression (Fisher 1971)

\[ C_v^i / k = (T^*)^{-1} \{ \langle (\delta U_0^* U_0^*)^2 \rangle + \langle (U_0^* U_\text{int}^*)^2 \rangle \} + (T^*)^{-1} \{ \langle U_\text{int}^* \rangle - \langle U_0^* \rangle \langle (\delta U_0^* U_\text{int}^*)^2 \rangle + \langle (\delta U_0^* U_\text{int}^* U_\text{int}^*)^2 \rangle \}, \]

(25)

where the shorthand notation

\[ \langle (\delta X Y) \rangle = \langle XY \rangle - \langle X \rangle \langle Y \rangle \]

(26)

for the variances has been used for convenience.

The specific heat for methane was calculated using equation (25) and the results are plotted in Fig. 1, together with the experimental curve from the equation of state for comparison. Both the molecular dynamics results and those from the
equation of state are reported with respect to a common ideal-gas specific heat (Goodwin 1971). Agreement between our values and experiment is not good, but the difficulties inherent in the molecular dynamics should be taken into account. We have established that the addition of three-body and quantum terms to equation (25) tends to decrease the calculated $C_v$ at high densities, consequently improving the agreement with experiment. Unfortunately the amount of computation time required to obtain accurate values of these correlation terms is prohibitive. However, it can be argued that the basic difficulty in determining $C_v$ accurately arises from the assumption that a system containing only 108 molecules can be treated as infinite. The effects of this restriction are most apparent near the critical density ($\rho_c = 160·4$ kg m\(^{-3}\)). Upon approaching the critical region, a real system is known to show large thermal fluctuations, leading to anomalous behaviour in several thermodynamic properties. In particular, experimental results show that $C_v$ diverges weakly, as indicated by the curve in Fig. 1. Our system is not large enough to include this collective molecular behaviour correctly.

Table 2. Comparisons between internal specific heats calculated for canonical and microcanonical ensembles

<table>
<thead>
<tr>
<th>$\rho$ (kg m(^{-3}))</th>
<th>$T$ (K)</th>
<th>$C_v/Nk$ canon.</th>
<th>$C_v/Nk$ mcanon.</th>
<th>$\rho$ (kg m(^{-3}))</th>
<th>$T$ (K)</th>
<th>$C_v/Nk$ canon.</th>
<th>$C_v/Nk$ mcanon.</th>
</tr>
</thead>
<tbody>
<tr>
<td>440·9</td>
<td>121·5</td>
<td>0·619</td>
<td>1·049</td>
<td>192·4</td>
<td>196·7</td>
<td>0·419</td>
<td>0·580</td>
</tr>
<tr>
<td>151·4</td>
<td>0·570</td>
<td>0·915</td>
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<td>213·0</td>
<td>0·385</td>
<td>0·517</td>
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</tr>
<tr>
<td>347·4</td>
<td>172·8</td>
<td>0·474</td>
<td>0·690</td>
<td>171·0</td>
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<td>220·0</td>
<td>0·380</td>
<td>0·308</td>
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<tr>
<td>258·7</td>
<td>202·8</td>
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</tr>
</tbody>
</table>

In this context, the paper by Lebowitz et al. (1967) on (in part) fluctuations in molecular dynamics calculations is relevant, since they discuss the analysis of machine results from various statistical mechanical ensembles. In our work we have established a microcanonical ensemble, but the expression (25) for the specific heat is strictly that for a canonical ensemble. We have, therefore, made the usual assumption that the two ensembles are thermodynamically equivalent. However, this assumption may not hold for the specific heat, as can be shown by the following argument. Let us assume for convenience that $C_v^0 = \frac{1}{2}Nk$ and $U^* = U^*_0$, so that for the canonical ensemble

$$C_v/Nk = \frac{1}{2} + (NT^*)^{-1}\langle(\delta U^*_0 U^*_0)^2\rangle.$$  \hspace{1cm} (27)

Lebowitz et al. have derived the corresponding expression for a microcanonical ensemble, namely

$$C_v/Nk = \frac{1}{2}\{1 - \frac{1}{3}(NT^*)^{-1}\langle(\delta U^*_0 U^*_0)^2\rangle\}.$$ \hspace{1cm} (28)

We have calculated $C_v^0$ from these two equations and the results are shown in Table 2. It is seen that the two calculations disagree by from 20% to 50%, which is felt to be outside our estimate of precision on the variance $\langle(\delta U^*_0 U^*_0)^2\rangle$. The results of Table 2 therefore lend support to the suggestion that the specific heat cannot be estimated properly from a system of 108 particles.
Conclusions

The molecular dynamics calculations of the thermodynamic properties of methane using a spherical $m$-6-8 potential are generally successful and complement the previous investigations of the dilute gas properties (Hanley and Klein 1972) and the dense fluid self-diffusion coefficient (Hanley and Watts 1975). The molecular dynamics method is not very satisfactory when applied to the specific heat, but it can be argued that this is a consequence of working with a small system.

Acknowledgments

This work was partially supported by the Office of Standard Reference Data (U.S.). H.J.M.H. is grateful for the kind hospitality of the Australian National University and for the help and encouragement of the members of the Diffusion Research Unit and the Computer Centre.

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Manuscript received 3 October 1974