

# Thermodynamics of homonuclear diatomic fluids from the angular median potential

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The use of the angular median potential as a temperature-independent spherical reference system for approximating molecular fluids is tested for its predictions of thermodynamics. Calculations have been carried out for a wide range of homonuclear diatomics with continuous atom-atom potentials believed to be representative of the full range of simulation data available for such systems. The results for the pressure are surprisingly good both in the detonation regime and around the triple point. In the latter case, however, the internal energies for highly elongated molecules with attractive potential wells are considerably too positive. Comparison with other perturbation theories indicates that the median reference system gives better pressures but poorer energies than RAM, and that in many cases, especially for purely repulsive potentials, it gives results of comparable accuracy to those obtained with nonspherical reference systems.

## I. INTRODUCTION

In a recent paper<sup>1</sup> Lebowitz and Percus proposed that the thermodynamic properties of a fluid of symmetric molecules interacting through an angle dependent potential  $v(R, \Omega_1, \Omega_2)$  be approximated by those of a fluid with a spherical potential  $w(R)$  equal to the angular median of  $v$ . Here  $R = |\mathbf{R}|$  is the distance between the centers of symmetry of two molecules while  $\Omega_1$  and  $\Omega_2$  define the orientations of the molecules relative to  $\mathbf{R}$ .  $w(R)$  may be defined by the relation<sup>1</sup>

$$\int d\Omega_1 \int d\Omega_2 \operatorname{sgn}[v(R, \Omega_1, \Omega_2) - w(R)] = 0 \quad (1)$$

or, since it is well known that the median minimizes the sum of absolute deviations, we may state that the potential  $w(R)$  is that  $W(R)$  which minimizes

$$\int d\Omega_1 \int d\Omega_2 |v(R, \Omega_1, \Omega_2) - W(R)|.$$

This prescription was shown<sup>1</sup> to work extremely well for a dense fluid of hard dumbbells with moderate elongations.

The suggestion for this type of sphericalization was based upon the work of Shaw *et al.*<sup>2</sup> who found, for site-site models of nitrogen, spherical reference potentials closely related to the median which work extremely well at very high temperatures and pressures and also quite well near the triple point. Gray and Joslin<sup>3</sup> subsequently found the median potential to be rather good for predicting second virial coefficients of diatomic Lennard-Jones molecules more elongated than "nitrogen."

As in Refs. 2 and 3, we restrict attention in the present note to symmetric (nonpolar) diatomic molecules interacting through continuous site-site potentials. (Hard-core systems are described in a separate paper.)<sup>4</sup> We make a systematic

examination of the usefulness of the median idea in predicting liquid thermodynamic properties for several different site-site interactions and for various elongations. The results are assessed against simulation data representative of the full range available (both in terms of nonsphericity and of thermodynamic states) and are also compared with other theoretical approaches.

In order to fix notation, we now define the interaction potentials considered here. Denoting the intramolecular site-site distance by  $l$  in all cases, the orientational vectors  $\Omega_i$  may be taken along the molecular axes so that

$$\begin{aligned} v(R, \Omega_1, \Omega_2) &= \sum_{\alpha=1}^2 \sum_{\beta=1}^2 \psi(r_{\alpha\beta}) \\ &= \sum \psi(|\mathbf{R} \pm \frac{1}{2} l \Omega_1 \pm \frac{1}{2} l \Omega_2|). \end{aligned} \quad (2)$$

Here  $\psi(r)$  is the site-site potential and the first summation is over all pairs of atoms in the two molecules which corresponds, in the second summation, to all possible  $+$ ,  $-$  pairs in the argument. We shall consider four different choices of  $\psi(r)$ :

The diatomic exponential-six (E6) molecule is given by

$$\psi_E(r) = \frac{\epsilon}{\alpha - 6} \left[ 6 \exp\left\{\alpha\left(1 - \frac{r}{r_m}\right)\right\} - \alpha\left(\frac{r_m}{r}\right)^6 \right] \quad (3)$$

and the diatomic Lennard-Jones (LJ) molecule by

$$\psi_{LJ}(r) = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6]. \quad (4)$$

In both of these,  $\epsilon$  represents the depth of the attractive well the minimum of which occurs at  $r = r_m$  for  $\psi_E(r)$  and at  $r = 2^{1/6}\sigma$  for  $\psi_{LJ}(r)$ .

The two remaining choices of  $\psi(r)$  are both purely repul-

sive. Choosing the repulsive part of the Lennard-Jones potential

$$\psi_R(r) = \begin{cases} \psi_{LJ}(r) + \epsilon, & r < 2^{1/6}\sigma \\ 0, & r > 2^{1/6}\sigma \end{cases} \quad (5)$$

gives the RLJ molecule, and with the inverse 12th power potential

$$\psi_P(r) = \epsilon(l/r)^{12} \quad (6)$$

we shall denote the resulting molecule by  $P$ . Notice that  $\psi_E$ ,  $\psi_{LJ}$ , and  $\psi_R$  all contain intrinsic length scales, whereas  $\psi_P$  has none. We are therefore free to choose the arbitrary scaling length in  $\psi_P$  to be  $l$  with the resulting advantage that all properties of  $P$  molecules for arbitrary thermodynamic states and elongations may be obtained by simple scaling from the properties for a single elongation. Thus, in the present approximation, a single median potential is sufficient for all  $P$  molecules, whereas a different median potential is necessary at each value of  $l$  for the other three interaction potentials considered.

The remainder of this paper is organized as follows: In Sec. II we give a brief description of computational details for finding the median potential and thermodynamic properties. After presentation and discussion of the numerical results in Sec. III, our conclusions are summarized in Sec. IV.

## II. NUMERICAL CALCULATIONS

### A. The median potential

For linear molecules we may take for the orientational vectors  $\Omega_i = (\theta_i, \phi_i)$ ,  $i = 1, 2$ , where  $\theta_i$  and  $\phi_i$  are the usual polar coordinates. To calculate the angular median for *symmetric* linear molecules, it suffices to consider the three-dimensional angular region  $\mathcal{D}$  defined by

$$-1 \leq \mu_1 \leq 1, \quad 0 \leq \mu_2 \leq 1, \quad 0 \leq \phi \leq \pi/2,$$

where  $\mu_i = \cos \theta_i$  and  $\phi = \phi_2 - \phi_1$ . The four site-site distances may be expressed in terms of  $R, l, \mu_1, \mu_2$  and

$$\Omega_1 \cdot \Omega_2 = \cos \theta_1 \cos \theta_2 + \sin \theta_1 \sin \theta_2 \cos \phi.$$

We partition  $\mathcal{D}$  into cells of equal size ( $\Delta\mu_1, \Delta\mu_2, \Delta\phi$ ) and, for a fixed centers separation  $R$ , evaluate  $v(R, q_j)$  at points  $q_j$ , one in each cell.  $q_j$  is picked using a pseudo-random uniform distribution (in each coordinate) over the  $j$ th cell.

We select a range  $v_0 \leq v \leq v_M$  of potential values (wide enough to include the median value) and divide it into  $M$  "bins"

$$B_m: v_{m-1} \leq v \leq v_m \quad (1 \leq m \leq M),$$

where  $v_m = v_0 + (m/M)(v_M - v_0)$ . In addition we define the two overflow bins

$$B_0: v < v_0$$

and

$$B_{M+1}: v > v_M.$$

For each cell  $j$  we add  $\pi^{-1} \Delta\mu_1 \Delta\mu_2 \Delta\phi$  to the bin  $B_m$  ( $0 \leq m \leq M+1$ ) such that  $v(R, q_j) \in B_m$ . When this has been done for all the cells, the quantity  $f_m$  in the bin  $B_m$  represents (within statistical error) the fraction of the volume of  $\mathcal{D}$  for

which  $v(R, \mu_1, \mu_2, \phi) \in B_m$ . Then the median potential  $w(R)$  satisfies

$$v_{n-1} \leq w \leq v_n$$

for  $n$  such that

$$s_{n-1} \leq \frac{1}{2} \leq s_n, \quad s_n = \sum_{m=0}^n f_m$$

and we linearly interpolate to obtain the estimate

$$w = v_{n-1} + \frac{(\frac{1}{2} - s_{n-1})(v_n - v_{n-1})}{f_n}. \quad (7)$$

After a crude search for  $w$  (during which  $[v_0, v_M]$  may have to be raised or lowered accordingly as  $f_{M+1} > \frac{1}{2}$  or  $f_0 > \frac{1}{2}$ ), an approximate median potential, say  $w^*$ , is found. To obtain our final value for  $w$ , we then set

$$v_0 = 0.95 w^*, \quad v_M = 1.05 w^*, \quad M = 200,$$

$$\Delta\mu_1 = \Delta\mu_2 = \frac{1}{24}, \quad \Delta\phi = \pi/24,$$

and take the mean from five separate realizations of the pseudo-random distribution. This repetition also allows an estimation of the statistical error which, except where  $w(R)$  falls steeply through zero, is never greater than 1%. Other than at centers separations where  $v(R, \mu_1, \mu_2, \phi)$  can be steeply repulsive, the statistical error is usually considerably less than 1%.

For a single value of  $R$ , the whole procedure for finding  $w(R)$  takes less than one minute of CPU time on a VAX-11/780 in the case of LJ molecules. We computed  $w(R)$  at several different values of  $R$  (up to 60 for some of the potentials considered) and used a cubic spline fit to interpolate between these. Whenever necessary, the long range part of the median potential was very accurately represented by a three term linear least squares fit with a choice of fitting functions appropriate to the asymptotic behavior  $w(R) \sim 4\psi(R)$ ,  $R/l \gg 1$ . On the other hand, the finite range of the median potential for a RLJ molecule was easily obtained from the median hard sphere diameter for a hard dumbbell molecule of equivalent elongation. Such median diameters are given in Ref. 4.

### B. Thermodynamics for the median potential

Having obtained  $w(R)$ , several different existing procedures could be used to calculate thermodynamic properties for it.<sup>5</sup> We chose Ross' procedure<sup>6</sup> for its simplicity and also because it seems to be accurate both near the triple point and in the high temperature, high pressure detonation regime. We sketch the method which consists of an empirical modification of the variational principle of Mansoori and Canfield<sup>7</sup> and Rasaiah and Stell<sup>8</sup> based on the Gibbs-Bogoliubov inequality.<sup>9</sup>

One starts with the expression

$$\frac{A^u}{Nk_B T} = \frac{\eta(4-3\eta)}{(1-\eta)^2} + \frac{2\pi\rho}{k_B T} \int_d^\infty w(R) g_{HS}^{(PY)}(R/d; \eta) \times R^2 dR - (\frac{1}{2}\eta^4 + \eta^2 + \frac{1}{2}\eta), \quad (8)$$

where  $A^u/N$  represents an approximate upper bound for  $A/N$ , the excess Helmholtz free energy per particle of the median potential fluid of number density  $\rho$  at temperature  $T$ ,  $d$  is a hard sphere (HS) diameter,  $\eta = (\pi/6)\rho d^3$  and  $g_{HS}^{(PY)}$  is the cor-

responding HS radial distribution function in the Percus–Yevick (PY) approximation.<sup>10</sup> On the right-hand side of Eq. (8), the first term represents  $A_{HS}/Nk_B T$  as given by Carnahan and Starling<sup>11</sup> while the first two terms together would give the Gibbs–Bogoliubov inequality if  $g_{HS}^{(PY)}$  were replaced by the exact  $g_{HS}$ . Ross' empirical correction consists of the use of  $g_{HS}^{(PY)}$  together with the addition of the third term. The variational approximation to  $A/Nk_B T$  is obtained by minimizing the right-hand side of Eq. (8) with respect to  $d$  for each thermodynamic state  $(\rho, T)$ . At minimization the integral term in Eq. (8) represents  $U/Nk_B T$ , where  $U$  is the excess internal energy, but the pressure  $p$  must be found by numerical differentiation along an isotherm

$$\frac{p}{\rho k_B T} = 1 + \rho \left( \frac{\partial}{\partial \rho} \right)_T \left( \frac{A}{Nk_B T} \right). \quad (9)$$

Many previous variational calculations in this field have been for potentials which were sums of exponential, Yukawa, and inverse power terms. The use of Laplace transform techniques in conjunction with the Wertheim–Thiele analytic solution of the PY approximation for HS<sup>12,13</sup> then facilitates evaluation of the integral in Eq. (8).<sup>7,14,15</sup> Shaw *et al.*<sup>2</sup> were indeed able to fit their spherulized potentials by exponential-six expressions and, in the course of the present work, we found that for short LJ molecules the important part of  $w(R)$  was well fitted by a sum of three Yukawa terms. Since we were, however, unable to obtain similar fits for the more elongated molecules, all of the numerical results reported in the following section were calculated using direct numerical integration. By generating values of  $g_{HS}^{(PY)}$  with the very efficient Perram algorithm<sup>16</sup> the computations can still be made reasonably fast.

Ross<sup>6</sup> only tested his procedure for (atomic) Lennard–Jones, exponential-six and inverse power potentials so that its validity for our median potentials may be questioned. (The same doubt would arise for the possible alternative methods<sup>5</sup> of obtaining median fluid thermodynamics.) For the median-like potentials of Shaw *et al.*,<sup>2</sup> however, the Ross procedure was found to be accurate to  $\sim 1\%$  by comparison with molecular dynamics simulations. A similar comparison for the median potential of a highly elongated E6 diatomic ( $l/r_m = 0.6288$ ) still found an accuracy of  $\sim 3\%$  (J. D. Johnson, private communication). We are therefore confident that the median fluid thermodynamic results reported below are sufficiently accurate to justify our statements concerning how well the median fluids represent the thermodynamic properties of the corresponding molecular fluids.

### III. RESULTS AND DISCUSSION

#### A. Comparison to simulations

Before describing our main results we note that the calculations of Shaw *et al.*<sup>2</sup> for E6 with  $l/r_m = 0.3028$  were carried out using a potential which is close but not identical to the median potential. The accuracy of thermodynamics which we obtained with the median potential is almost as good as that claimed by Shaw *et al.*<sup>2</sup> for their spherical potential, by comparison with their (rigid rotor) simulations.<sup>17</sup>

Our principal interest is in the LJ system since it has been most widely studied in simulations. We have carried

out calculations for all of the elongations at which simulations are available but show results only for three of these, which are, however, sufficiently indicative of the observed trends. The three have  $l/\sigma = 0.3292$ , a model of nitrogen,<sup>18</sup>  $l/\sigma = 0.5471$ , a model of bromine<sup>19</sup> or chlorine<sup>20</sup> and  $l/\sigma = 0.793$ , a model of carbon dioxide.<sup>20</sup>  $l/\sigma = 0.5471$  is probably not the best elongation available for either bromine or chlorine<sup>20</sup> but we are here concerned only with comparison of theory to simulation and not with the underlying real systems. Therefore we chose to present results for this particular elongation solely because of the large amount of simulation data and other approximate data available for it.

Figure 1 shows the median potentials for the shortest and longest LJ molecules we consider alongside four times the site–site potential. Clearly as  $l/\sigma$  increases the position of the potential minimum moves to larger separations and the well depth decreases markedly. In addition, the repulsive part of  $w(R)$  becomes steeper. We also remark that there seems to be a discontinuity in  $dw/dR$  near the minimum. This is most obvious for large  $l/\sigma$  but we believe that it exists for any nonzero  $l$ .

Figures 2–4 show our thermodynamic results in terms of the dimensionless quantities which have become standard for LJ molecules:  $T^* = k_B T/\epsilon$ ,  $\rho^* = \rho\sigma^3$ ,  $p^* = p\sigma^3/\epsilon$ ,  $U^* = U/N\epsilon$ , and  $E^* = U^* + \frac{3}{2}T^*$ . The simulation results shown come from Tables II and IV of Wojcik *et al.*<sup>21</sup> who conveniently summarize all available machine data for LJ molecules. Since these results are based on linear interpolation along isochores but the range of temperatures studied is not given, we cannot rule out the possibility that some of the

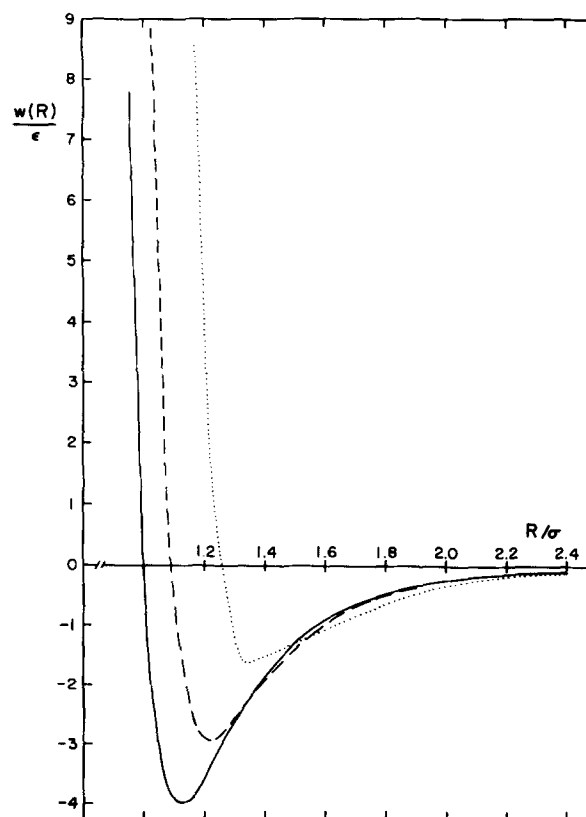


FIG. 1. Median potentials for LJ diatomics: —:  $l/\sigma = 0$  [i.e.,  $4\psi(R)$ ]; - - -:  $l/\sigma = 0.3292$ ; ...:  $l/\sigma = 0.793$ .

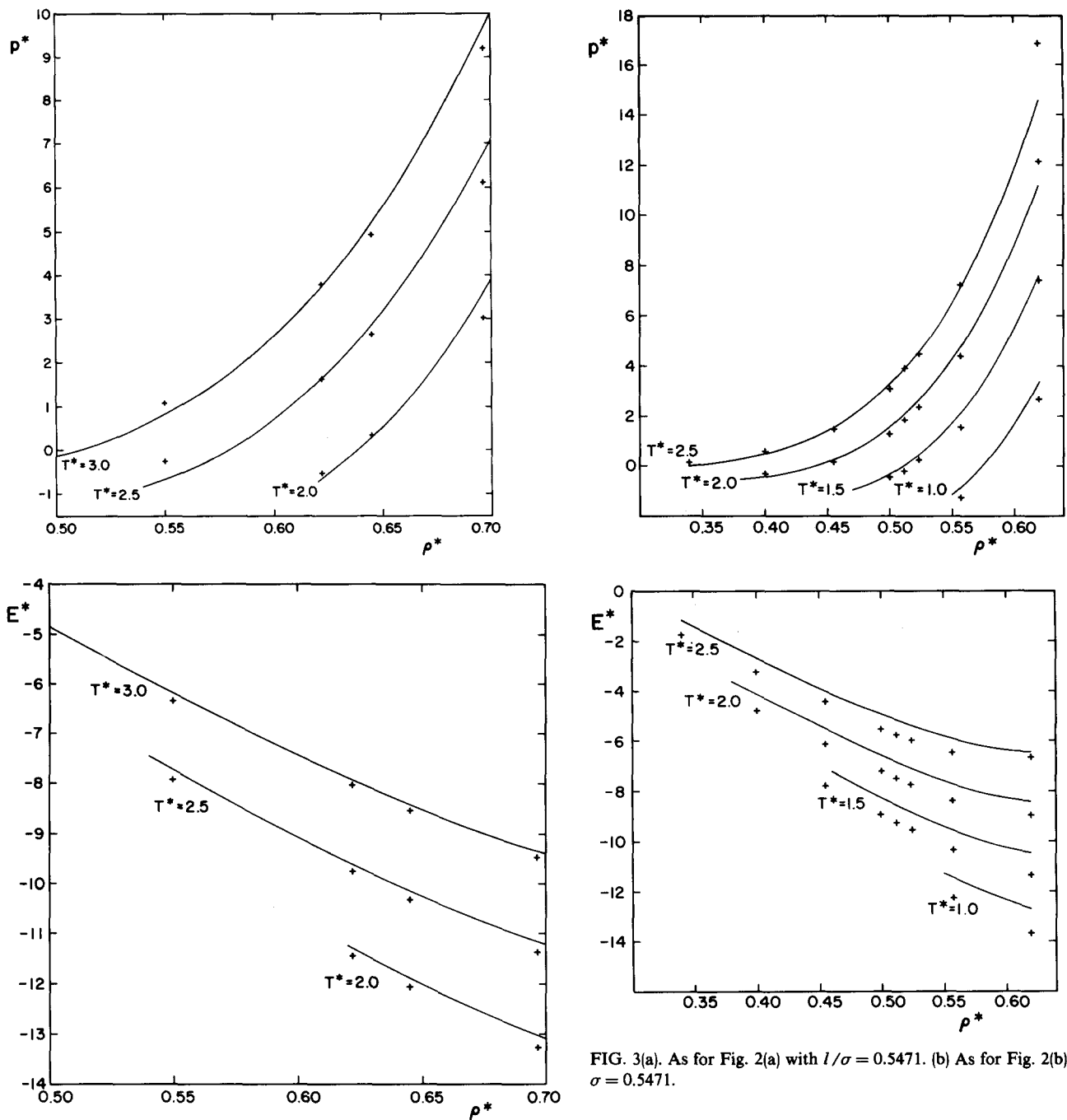


FIG. 3(a). As for Fig. 2(a) with  $l/\sigma = 0.5471$ . (b) As for Fig. 2(b) with  $l/\sigma = 0.5471$ .

FIG. 2(a). Pressures for LJ diatomics with  $l/\sigma = 0.3292$ : —: median (MED); +: simulation (SIM) (Ref. 21). (b) Internal energies for LJ diatomics with  $l/\sigma = 0.3292$ : —: MED; +: SIM (Ref. 21).

high pressure simulation results shown in Figs. 2–4 may be unreliable extrapolations.

The pressures shown in Figs. 2(a)–4(a) show some deterioration of accuracy with increasing elongation but this is not nearly as bad as the deterioration of the energy results [Figs. 2(b)–4(b)]. A plausible explanation for the poor energy results can be given in terms of the distribution of potential values shown in Fig. 5 for  $l/\sigma = 0.793$ ,  $R/\sigma = 1.20$ . This value of  $R$  is smaller than the HS diameters determined by the Ross procedure for this LJ molecule and yet nearly 40% of potential values in the angular domain  $\mathcal{D}$  are negative. Thus a large number of negative energy configurations are

totally ignored in the median calculation and it is not surprising that  $E^*$  is too positive. The same effect is present to a smaller extent in the less elongated molecules. This is a manifestation of the inability of the median to handle important localized fluctuations of the potential. A more extreme example is provided by the hard dumbbell molecule. The addition of a sufficiently narrow (finite ranged) attractive well to this molecule does not affect its median potential *at all*.

We have seen that the median method works much better for E6 molecules at extremely high  $(\rho, T)$  than for LJ molecules at normal  $(\rho, T)$ . This, together with the fact<sup>1,4</sup> that the median works well for hard objects, strongly suggests that the deterioration in the normal liquid regime is due to the importance there (especially for the internal energy) of attractive forces. A natural test of this hypothesis was to apply the method to purely repulsive continuous atom–atom

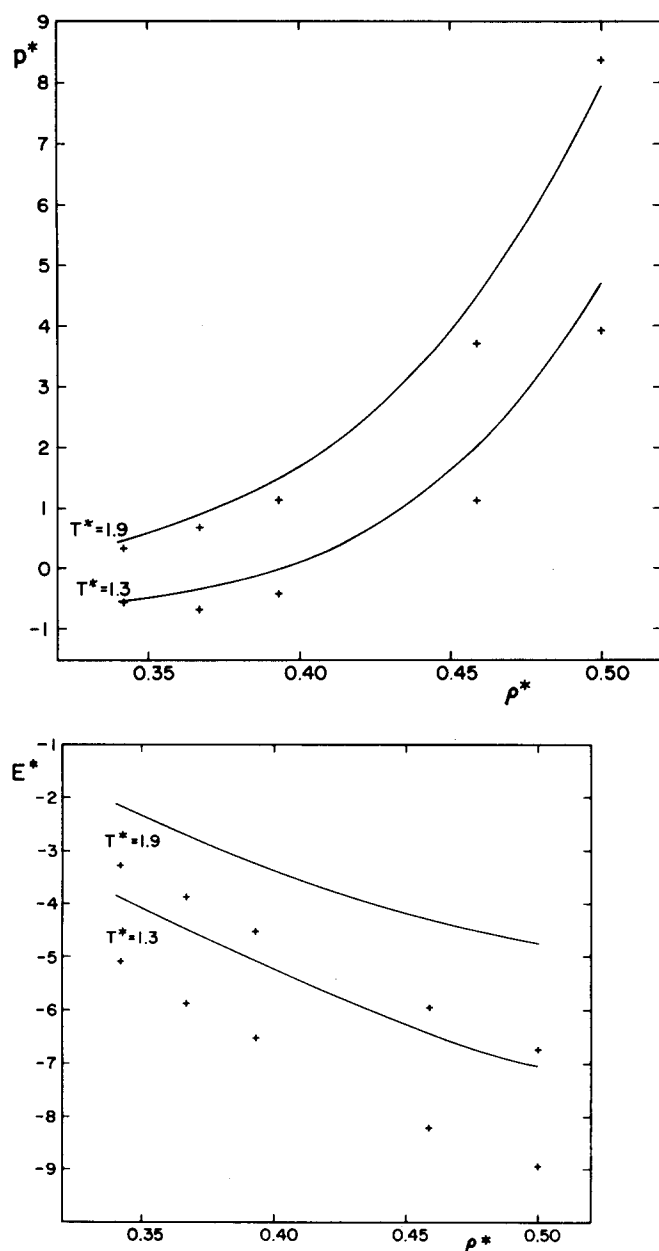


FIG. 4(a). As for Fig. 2(a) with  $l/\sigma = 0.793$ . (b) As for Fig. 2(b) with  $l/\sigma = 0.793$ .

potentials of which, to our knowledge, the only ones to have been simulated are the two mentioned in the Introduction.

For RLJ molecules, only three simulation states are available. Median results for these are shown along with the simulation data<sup>19</sup> in Table I. Trends in accuracy cannot be distinguished from just three states but the values of  $U^*$  seem to remain quite accurate even at fairly high  $l/\sigma$ . Indeed, except that  $p^*$  is clearly too high at the lowest temperature, the median results probably lie within the uncertainties of the simulation data.

The repulsions in E6 and RLJ molecules are very strong and so it is of interest to see how well the median method works for softer repulsions. Motivated partly by this consideration and also by the availability of a wider range of simulation data due to Few and Rigby<sup>22</sup> we applied the median method to  $P$  molecules. Our results are compared to simula-

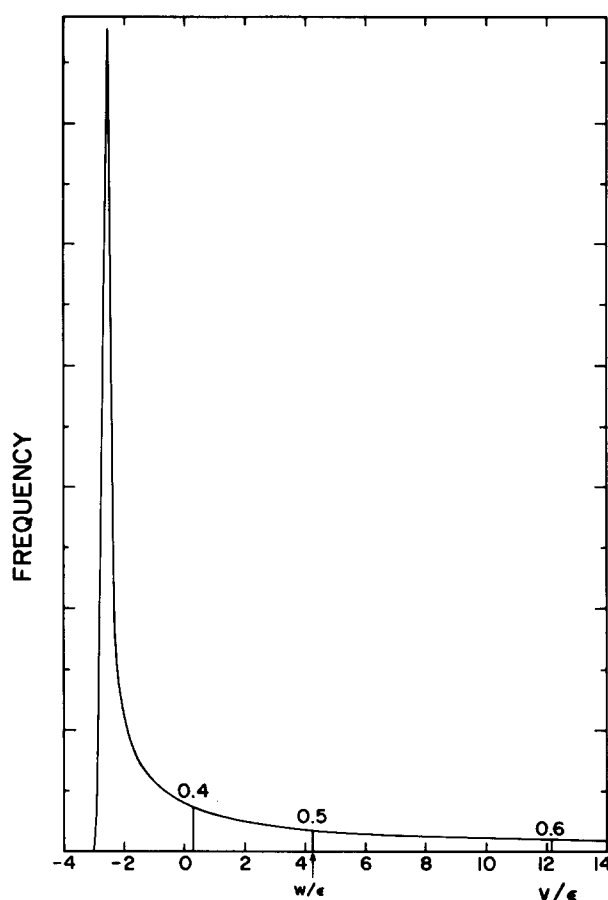


FIG. 5. Frequency distribution for potential energy values of the LJ diatomic with  $l/\sigma = 0.793$  at  $R/\sigma = 1.20$ . Cumulative fractions are indicated by vertical lines, that with 0.5 corresponding to the median potential  $w(R)$ . Frequency units are arbitrary.

tions in Fig. 6. We draw attention to the fact that, for good reasons,<sup>23</sup> we use different dimensionless units from those of Few and Rigby. Since we have no simple elongation ratio for  $P$  molecules, we must distinguish "elongated"  $P$  molecules by high values of  $\rho l^3$  and  $k_B T/\epsilon$ . The median results for  $P$  molecules are quite accurate for both isotherms simulated but less so for the more "elongated" case.

## B. Comparison to other perturbation theories

Thus far we have only compared median (MED) results with simulations but it is also of interest to compare MED with competing perturbation theories. We remark that, in the sense of equal ease of computation, the only truly competing reference system is the (spherical) angular mean potential.<sup>24</sup> However, this works so poorly for diatomic mole-

TABLE I. Comparison of simulation (SIM) (Ref. 19) and median (MED) results for RLJ pressures and excess internal energies.

$l/\sigma$	$\rho^*$	$T^*$	$p_{\text{SIM}}^*$	$p_{\text{MED}}^*$	$U_{\text{SIM}}^*$	$U_{\text{MED}}^*$
0.5471	0.524	2.18	12.69	12.69	2.48	2.38
	0.524	2.44	13.48	13.66	2.64	2.62
0.6288	0.500	1.28	8.56	8.92	1.58	1.61

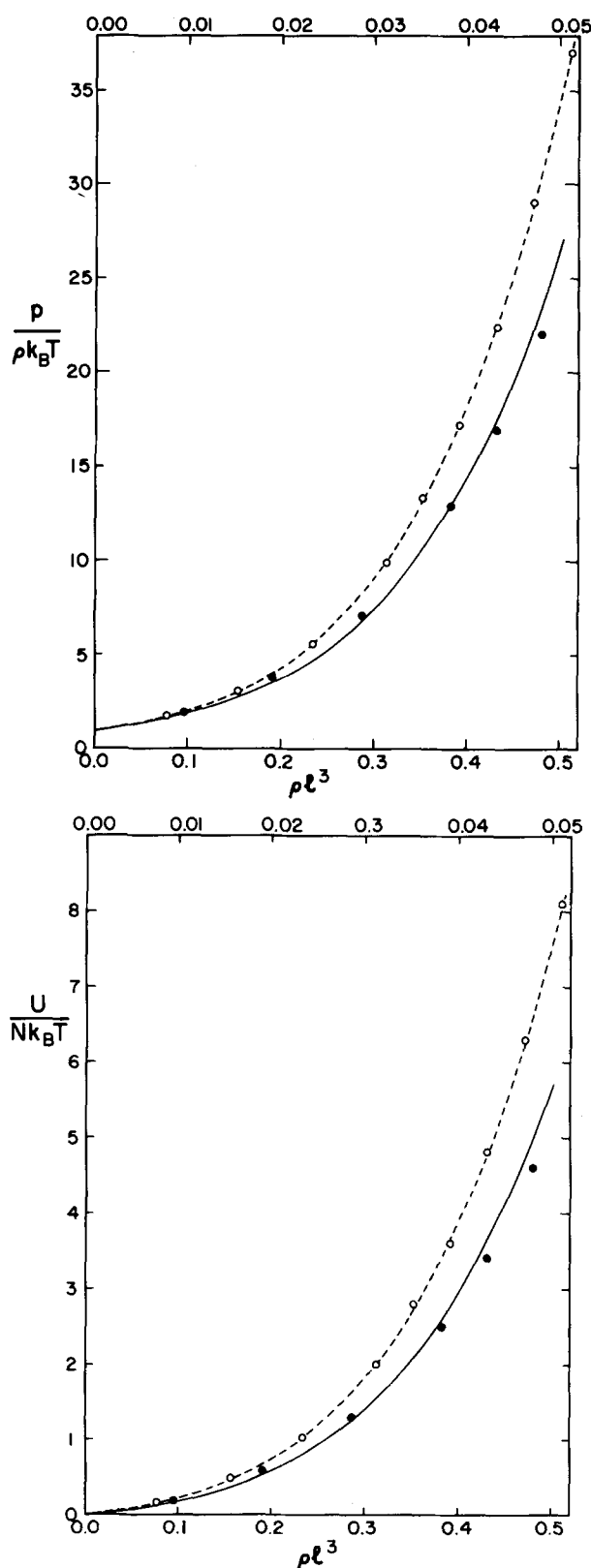


FIG. 6(a) Pressure of  $P$  diatomics for two isotherms.  $k_B T/\epsilon = 1$ : —: MED; ●: SIM (Ref. 22); lower density scale.  $k_B T/\epsilon = 1.678 \times 10^{-5}$ : - - -: MED; ○: SIM (Ref. 22); upper density scale. (b) Excess internal energies of  $P$  diatomics for the same two isotherms as in Fig. 6(a).

cules<sup>2,3,25</sup> that we shall not consider it here. Of greater interest are three other approaches which we outline briefly before making numerical comparisons.

Angle averaging of the Boltzmann factor yields a tem-

perature-dependent spherical reference potential  $v_T(R)$  defined by

$$\int d\Omega_1 \int d\Omega_2 [\exp\{-v(R, \Omega_1, \Omega_2)/k_B T\} - \exp\{-v_T(R)/k_B T\}] = 0. \quad (10)$$

Now commonly known as the reference averaged Mayer (RAM) potential,  $v_T(R)$  was first proposed by Cook and Rowlinson.<sup>26</sup> It was more recently reintroduced by Perram and White<sup>27</sup> and then formulated in a more general context by Smith.<sup>28</sup> A very comprehensive review of RAM is given by Smith and Nezbeda.<sup>25</sup> Due to the temperature dependence of  $v_T(R)$  it is much more difficult to compute thermodynamics for a wide range of  $\rho$  and  $T$  using RAM than using MED and this accounts for the sparse RAM thermodynamic data in the published literature. For the same reason, available RAM thermodynamic data were not obtained (as were our MED results and the WCA results discussed below) by differentiation of  $A/Nk_B T$  but rather from integrals involving the correlation functions. In this respect, the RAM and MED results are not *strictly* comparable but in the absence of other results we nevertheless make the comparison. It is probably fairest to compare MED (lowest order free energy expansion) to higher order RAM (correlation function expansion) results. We also point out that the accuracy currently obtainable from RAM is the consequence of trying many different versions of it and choosing the best.<sup>25</sup> Of particular relevance in the present context is the fact that early RAM calculations used the centers frame (CF) but that improved results were later obtained using the site frame (SF). In contrast, our present formulation of MED is a straightforward first guess using CF which may be amenable to later improvement.

The remaining two methods involve nonspherical reference systems which immediately give rise to difficulties in obtaining reference system properties. They constitute two different generalizations to molecular systems of the idea, due to Weeks *et al.* (WCA)<sup>29</sup> for atomic systems, of splitting the potential into its repulsive and attractive parts. Kohler *et al.*<sup>30</sup> suggested carrying out this split in the CF for each fixed  $(\Omega_1, \Omega_2)$ . Tildesley,<sup>31</sup> on the other hand, carried out a WCA split of the site-site potential. In both cases, the properties of the repulsive reference system are ultimately obtained from those of hard dumbbells. Following Quirke and Tildesley<sup>32</sup> we denote these two methods WCA(CF) and WCA(SF), respectively. Both require considerably more computation than MED but while WCA(CF), like RAM and MED, is in principle applicable to any nonspherical molecule, WCA(SF) is fundamentally restricted to treating site-site molecules.

For LJ molecules, we expect that the WCA theories will both yield better results than MED at high  $l/\sigma$  and this is seen to be true for WCA(SF) from Table II. That it is also true for WCA(CF) can be seen by comparing Fig. 3 of Fischer<sup>34</sup> with Fig. 4(a) of the present paper. More surprisingly, it appears that at  $l/\sigma = 0.3292$  MED is of comparable accuracy to the WCA methods at least for pressures and internal energies. There are, however, some simulation results for free energies<sup>35</sup> and it can be seen from Table III that

TABLE II. Pressures and excess internal energies for LJ diatomics. The orders of the various RAM calculations are indicated by subscripts. In the bottom row, /SIM indicates that the radial distribution function of the RAM fluid was obtained by simulation. (Otherwise it was found in the PY approximation.) RAM(CF)<sub>2</sub><sup>\*</sup> is used to denote the  $F_{CF}^{2*}$  results of Ref. 32.

$l/\sigma$	0.3292		0.3292		0.5471		0.5471		0.5471		0.793	
$\rho^*$	0.66		0.6964		0.3002		0.524		0.524		0.422	
$T^*$	1.791		1.55		2.31		1.23		2.26		1.345	
	$p^*$	$U^*$	$p^*$	$U^*$	$p^*$	$U^*$	$p^*$	$U^*$	$p^*$	$U^*$	$p^*$	$U^*$
SIM <sup>a,b</sup>	-0.06	-17.64	+0.30	-18.60	-0.14	-7.18	-0.87	-13.58	+3.31	-12.50	+0.14	-10.54
WCA(SF) <sup>b</sup>	+3.1	-17.1							+3.6	-12.4	-0.0	-10.5
MED	-0.12	-17.48	+0.45	-18.66	-0.22	-6.45	-0.80	-12.85	+3.68	-11.86	+0.78	-9.34
RAM(SF) <sub>0</sub> <sup>b</sup>	+1.4	-16.9							+3.2	-12.9	-2.1	-10.7
RAM(CF) <sub>0</sub> <sup>b,c</sup>	-3.0	-17.9			-0.59	-7.07			-0.1	-13.0	-1.8	-10.8
RAM(CF) <sub>1</sub> <sup>b,c</sup>	-3.7	-16.6	-4.12	-17.67	-0.56	-6.79	-3.65	-11.85	-0.8	-11.5	-1.8	-9.2
RAM(CF) <sub>2</sub> <sup>*</sup>	-1.5	-17.7							+1.2	-12.9	-1.2	-10.8
RAM(CF/SIM) <sub>1</sub> <sup>c</sup>			-4.02	-17.87					-0.43	-11.55		

<sup>a</sup>Reference 19.

<sup>b</sup>Reference 32.

<sup>c</sup>Reference 33.

the WCA theories give markedly better values for  $A/Nk_B T$  itself. The accuracy of MED for  $p^*$  and  $U^*$  can be attributed to its remarkably constant and quite small error for  $A/Nk_B T$ . Again from Table II we see that, compared to the most accurate of the RAM results, MED gives better pressures but poorer energies.

We have already seen for RLJ molecules that MED is in good agreement with simulations and so it is no surprise to find (Table IV) that this agreement is better than for the other perturbation theories, apart from WCA(SF) which is especially suited to RLJ. The observation that WCA(CF) is not very good for RLJ suggests that its accuracy for LJ may be due to a fortuitous cancellation of errors arising from its treatments of the repulsive reference system and of the attractive perturbation.

For RLJ, only zero order RAM results are available and RAM(SF) is clearly better than RAM(CF). The RAM(SF) calculations of Nezbeda and Smith<sup>36</sup> use simulation input for the site-site radial distribution function while those of Quirke and Tildesley<sup>32</sup> are free of simulation input. The superiority of the latter result, admittedly only for a single thermodynamic state, leads us again to suspect a partial cancellation of errors occurring in the simulation-free RAM(SF) calculation due to the approximate treatment of

TABLE III. Excess free energies for LJ diatomics with  $l/\sigma = 0.3292$ . For the last state, a second order RAM calculation (Ref. 32) yields  $A/Nk_B T = -7.60$ .

$\rho^*$	$T^*$	$A/Nk_B T$			
		SIM <sup>a</sup>	MED	WCA(SF) <sup>b</sup>	WCA(CF) <sup>c</sup>
0.6	3.0	-2.02	-2.15	-2.06	-2.02
0.7	3.0	-1.71	-1.86	-1.75	-1.70
0.7	2.0	-4.66	-4.79	-4.66	-4.67
0.7	1.55	-7.35	-7.47	-7.34	-7.39

<sup>a</sup>Reference 35.

<sup>b</sup>Reference 32.

<sup>c</sup>Reference 34.

the RAM potential fluid and to its representation of the true molecular fluid. No matter which of these versions of RAM we consider, MED is still superior in treating the RLJ systems that have been simulated.

#### IV. CONCLUSIONS

Because the median potential is density and temperature independent, MED provides a means of obtaining a wide range of thermodynamic results from a relatively small amount of computation. For purely repulsive potentials, or for the detonation regime where attractions are unimportant, MED works very well. When the potential has an attractive part whose effect is large, MED still works well at small elongations but at larger elongations the pressure results deteriorate somewhat and the negative contribution to the internal energy is severely underestimated. A possible remedy for this situation, without going to higher order terms, might be to take the median separately for the repulsive and attractive parts of the potential. We are currently exploring this.

TABLE IV. Pressures and excess internal energies for RLJ diatomics. All RAM results shown are zero order.

$l/\sigma$	0.5471		0.5471		0.6288	
$\rho^*$	0.524		0.524		0.500	
$T^*$	2.18		2.44		1.28	
	$p^*$	$U^*$	$p^*$	$U^*$	$p^*$	$U^*$
SIM <sup>a</sup>	12.69	2.48	13.48	2.64	8.56	1.58
WCA(SF) <sup>b</sup>	12.4	2.4				
WCA(CF) <sup>c</sup>	13.39				9.28	
MED	12.69	2.38	13.66	2.62	8.92	1.61
RAM(SF) <sup>b</sup>	12.6	2.4				
RAM(CF) <sup>b</sup>	9.3	1.7				
RAM(SF/SIM) <sup>d</sup>	13.1		13.7		9.1	

<sup>a</sup>Reference 19.

<sup>b</sup>Reference 32.

<sup>c</sup>Reference 34.

<sup>d</sup>Reference 36.

Another shortcoming of MED is its inability to treat successfully potentials where the only nonspherical part is multipolar, although the situation is less clear for multipolar potentials with nonspherical short range repulsions. For example, the median potential for dipolar hard spheres is obviously just the hard sphere potential,<sup>3</sup> whereas for dipolar hard dumbbells the median potential is the median hard sphere corresponding to the (neutral) dumbbell<sup>4</sup> plus a finite-ranged repulsive tail.

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We feel that it is better not to use arbitrary lengths in our dimensionless densities and so prefer to use  $\rho l^3$  since  $l$  is the only physically meaningful length scale associated with a  $P$  molecule.

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