Limitations on the usefulness of the angular median
and related potentials

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The use of the angular median and related effective spherical potentials to predict thermodynamic properties of nonpolar homonuclear diatomic liquids has recently been shown to be efficient and accurate. Here we compare the results obtained from median-like methods for some other molecular liquids with simulation data. We find impressive agreement for linear triatomic molecules but results for tetrahedral molecules and for the overlap potential are very poor. The characteristic shape of potential energy frequency distributions at fixed separations is suggested as a criterion for the success or otherwise of the median potential.

1. INTRODUCTION

The prediction of equilibrium properties of molecular liquids by currently available perturbation theories is not, in general, very simple or accurate. There are two notable exceptions: the use of Padé approximants for the free energy of molecules whose sole anisotropy is multipolar [1, 2] and the treatments of non-polar homonuclear diatomics based upon a hard dumbbell reference system [3–6]. Even here the prediction of correlation functions is much less satisfactory than that of thermodynamics.

A recent innovation has been the successful use of the angular median potential [7, 8] and related potentials [8, 9] to reproduce the thermodynamics of some model molecules. We emphasize that even where these potentials give extremely accurate thermodynamic results, they are very poor at predicting structural properties [10, 11]. Also, although these potentials could in principle be used as
reference systems in perturbation theories; no perturbation corrections have actually been calculated. There are at least two good reasons for continuing this approach of regarding the median as an effective spherical potential (ESP) rather than a spherical reference system. First, the arguments which led to the median potential [8] suggest that, for a natural path in potential space, the perturbation corrections should be small. Second, for any moderately realistic potential, the perturbation corrections will be very hard to calculate. A concrete example of this is discussed in more detail below.

In fact, apart from some hard objects [12, 13], the only molecular models for which the median-like methods have been tested are nonpolar homonuclear diatomics [8, 14, 9, 15]. This is natural since such molecules have been extensively simulated but, as a result, the methods have not really added any new class of theoretically 'understood' potential models; rather they enable thermodynamic results of comparable accuracy to those of references [3–6] to be obtained from a much simpler and faster computation. One of the major motivations for seeking this greater simplicity was to facilitate the study of complicated mixtures and a start has been made in this direction [16].

It has already been noticed that median-like potentials are not useful for multipolar molecules [17, 14]. In this paper, we address the question of whether such potentials are useful for anything other than diatomic molecules. In §2 we consider in some detail polyatomic molecules and the so called overlap potential, as well as remarking briefly on multipolar potentials. The results are tentatively interpreted in terms of frequency distributions (at fixed separation) of potential values in §3 followed by concluding remarks in §4.

2. THERMODYNAMIC RESULTS

(a) Polyatomic (site-site) molecules

Consider a symmetric m-atomic molecule $XY_m$ (for example CS$_2$, CF$_4$ or SF$_6$) with Lennard-Jones (LJ) atom–atom potentials

$$
\psi_{AB}(r) = 4\varepsilon_{AB} \left( \left( \frac{\sigma_{AB}}{r} \right)^{12} - \left( \frac{\sigma_{AB}}{r} \right)^{6} \right),
$$

(1)

Then the total intermolecular potential $\nu$ is determined by $m$, the $X-Y$ bond-length $l$, and six LJ parameters $\varepsilon_{XX}$, $\sigma_{XX}$, $\varepsilon_{XY}$, $\sigma_{XY}$, $\varepsilon_{YY}$, $\sigma_{YY}$. It is convenient to write

$$
\nu(R, \Omega^a, \Omega^b) = \nu_{XX}(R) + \nu_{XY}(R, \Omega^a, \Omega^b) + \nu_{YY}(R, \Omega^a, \Omega^b),
$$

(2)

where $\Omega^a, \Omega^b$ are the orientations of molecules $a$ and $b$ whose centres are separated by the vector $R$, and

$$
\nu_{XX}(R) = \psi_{XX}(R)
$$

(3)

$$
\nu_{XY}(R, \Omega^a, \Omega^b) = \sum_{i=1}^{m} \psi_{XY}(\|R + l\vec{n}_{i}^a\|) + \sum_{i=1}^{m} \psi_{XY}(\|R - l\vec{n}_{i}^b\|)
$$

(4)

$$
\nu_{YY}(R, \Omega^a, \Omega^b) = \sum_{i=1}^{m} \sum_{j=1}^{m} \psi_{YY}(\|R + l(\vec{n}_{i}^a - \vec{n}_{j}^b)\|).
$$

(5)

Here $\vec{n}_i$ is a unit vector along the $XY$ bond to $Y$ atom $k$ in molecule $c$. 
Table 1. Coefficients appearing in equation (8), the fit to the ESP $W(R)$ for linear triatomic $(m = 2)$ and tetrahedral $(m = 4)$ molecules.

<table>
<thead>
<tr>
<th>$m$</th>
<th>$AB$</th>
<th>$\nu$</th>
<th>$q_{0\nu}$</th>
<th>$q_{1\nu}$</th>
<th>$q_{2\nu}$</th>
<th>$q_{3\nu}$</th>
<th>$q_{4\nu}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>$XY$</td>
<td>12</td>
<td>4-000</td>
<td>20:7380</td>
<td>30:2628</td>
<td>$-14:3134$</td>
<td>$9:11776$</td>
</tr>
<tr>
<td>2</td>
<td>$XY$</td>
<td>6</td>
<td>4-000</td>
<td>4:63944</td>
<td>0:814756</td>
<td>$0:130504$</td>
<td>$-1:84746$</td>
</tr>
<tr>
<td>2</td>
<td>$YY$</td>
<td>12</td>
<td>4-000</td>
<td>41:4760</td>
<td>85:0292$^\dagger$</td>
<td>$-64:410$</td>
<td>$-22:0825$</td>
</tr>
<tr>
<td>2</td>
<td>$YY$</td>
<td>6</td>
<td>4-000</td>
<td>9:27888</td>
<td>$-0:267648$</td>
<td>$7:31992$</td>
<td>$-3:54689$</td>
</tr>
<tr>
<td>4</td>
<td>$XY$</td>
<td>12</td>
<td>8-000</td>
<td>176:000</td>
<td>1436:73</td>
<td>$7311:22$</td>
<td>$12694:4$</td>
</tr>
<tr>
<td>4</td>
<td>$XY$</td>
<td>6</td>
<td>8-000</td>
<td>40:000</td>
<td>91:8706</td>
<td>$187:104$</td>
<td>$-443:485$</td>
</tr>
<tr>
<td>4</td>
<td>$YY$</td>
<td>12</td>
<td>16-000</td>
<td>704:000</td>
<td>16698:8</td>
<td>$176835:0$</td>
<td>$2926440:0$</td>
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<tr>
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<td>$YY$</td>
<td>6</td>
<td>16-000</td>
<td>160:000</td>
<td>1111:00</td>
<td>$4594:88$</td>
<td>$-3666:91$</td>
</tr>
</tbody>
</table>

$^\dagger$ Allowing for a trivial factor of 4, these values do not correspond exactly to those given for homonuclear diatomics in [9]. This is because the $Y-Y$ elongation here slightly exceeds the maximum value for which the fit of [9] is valid.

The basic median procedure [7] uses an ESP $w(R)$ defined by

$$
\int d\Omega^a \int d\Omega^b \ \text{sgn} \ [w(R, \Omega^a, \Omega^b) - w(R)] = 0.
$$

(6)

It was found for elongated diatomics, however, that splitting $\nu$ into its repulsive and attractive parts before taking their individual medians and recombining these [9] improved agreement of thermodynamic results with simulations. For diatomics, the spherical potential obtained by taking separate medians of the $r^{-12}$ and $r^{-6}$ terms in the site–site potential proved most accurate and had the additional advantage of yielding a universal ESP for any elongation [9]. This and the use of a Laplace transform identity greatly reduced the computer time needed to calculate thermodynamic properties (see [16]).

Since we do not wish to prejudge the efficacy of potential splitting for other molecules on the sole basis of results for diatomics, we have carried out calculations with ESPs of three types:

(i) Basic median [equation (6)].

(ii) Separate medians of two expressions, the sums of all $r^{-12}$ and $r^{-6}$ terms.

(iii) Separate medians of four expressions, the sums of the $r^{-12}$ and $r^{-6}$ terms in $\nu_{XY}$ and $\nu_{YY}$, respectively (plus the trivial $\nu_{XX}$).

As in our previous work, we continue to use Ross' procedure [18] to obtain the thermodynamics of the sphericalized fluids. The calculations for type (i) are obvious generalizations of those in [14] and the ones for types (ii) and (iii) are obvious generalizations of those in [9].

In a physical sense, ESP type (ii) is most analogous to the splits used for diatomics but, because there are two atomic species in each molecule, it is only type (iii) which avoids recomputation of medians for different potential parameters. For a given basic molecular geometry (i.e. a given $m$), an ESP $W(R)$ of type (iii) can be obtained for arbitrary values of the parameters $\delta_{AB}$, $\sigma_{AB}$ as a linear
combination of just four universal functions. We have obtained fits to these functions of the same form as those given in [9] for diatomics:

\[
W(R) = 4\varepsilon_{XX} \left\{ \left( \frac{\sigma_{XX}}{R} \right)^{12} - \left( \frac{\sigma_{XX}}{R} \right)^{6} \right\} + 4\varepsilon_{XY} \left\{ \left( \frac{\sigma_{XY}}{l} \right)^{12} M_{XY12} \left( \frac{R}{l} \right) - \left( \frac{\sigma_{XY}}{l} \right)^{6} M_{XY6} \left( \frac{R}{l} \right) \right\} + 4\varepsilon_{YY} \left\{ \left( \frac{\sigma_{YY}}{l} \right)^{12} M_{YY12} \left( \frac{R}{l} \right) - \left( \frac{\sigma_{YY}}{l} \right)^{6} M_{YY6} \left( \frac{R}{l} \right) \right\},
\]

where

\[
M_{AB}(x) = x^{-v} (q_{AB}^{(0)} + q_{AB}^{(1)} x^{-2} + q_{AB}^{(2)} x^{-4} + q_{AB}^{(3)} x^{-6} + q_{AB}^{(4)} x^{-8}).
\]

The coefficients \(q_{AB}^{(i)}\) are given in table 1. We note that although our methods clearly can be applied to arbitrary values of \(\varepsilon_{XY}, \sigma_{XY}\), all simulated systems we consider satisfy the Lorentz–Berthelot rules

\[
\sigma_{XY} = \frac{1}{2}(\sigma_{XX} + \sigma_{YY})
\]

\[
\varepsilon_{XY} = (\varepsilon_{XX} \varepsilon_{YY})^{1/2}.
\]

Tildesley and Madden [19] have simulated a model of CS\(_2\) of the type considered above with \(l = 1.57\ \text{Å}, \ \sigma_{CC} = 3.35\ \text{Å}, \ \sigma_{SS} = 3.52\ \text{Å}, \ \varepsilon_{CC}/k_B = 51.2\ K, \ \varepsilon_{SS}/k_B = 183.0\ K. \) Although there have been other simulations of CS\(_2\) [20, 21] this is the only publication in which thermodynamic results have been given. Simulation and median results are compared in table 2. Clearly, as for diatomics, (i) gives energies that are much too high while (ii) and, more so, (iii) reduce this

Table 2. Comparison of median-based and simulation results for thermodynamics of a triatomic Lennard-Jones model of CS\(_2\) (model A of [19]). \(p\) represents the pressure and \(U\) the excess internal energy.

<table>
<thead>
<tr>
<th>(\rho (\text{g/cm}^{-3}))</th>
<th>(T (\text{K}))</th>
<th>(p\sigma_{SS}^2)</th>
<th>(k_B T/\varepsilon_{SS})</th>
<th>(p\sigma_{SS}^2/\varepsilon_{SS}) (upper row)</th>
<th>(U/N\varepsilon_{SS}) (lower row)</th>
<th>MD</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.09</td>
<td>395</td>
<td>0.376</td>
<td>2.158</td>
<td>+0.59</td>
<td>+0.01</td>
<td>-0.43</td>
</tr>
<tr>
<td>1.16</td>
<td>355</td>
<td>0.400</td>
<td>1.940</td>
<td>+0.77</td>
<td>+0.17</td>
<td>-0.39</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>-12.59</td>
<td>-14.32</td>
<td>-14.53</td>
</tr>
<tr>
<td>1.22</td>
<td>319</td>
<td>0.421</td>
<td>1.743</td>
<td>+0.98</td>
<td>+0.42</td>
<td>-0.29</td>
</tr>
<tr>
<td>1.26</td>
<td>298</td>
<td>0.435</td>
<td>1.628</td>
<td>+1.22</td>
<td>+0.72</td>
<td>-0.10</td>
</tr>
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<td></td>
<td></td>
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<td></td>
<td>-13.93</td>
<td>-15.92</td>
<td>-16.18</td>
</tr>
<tr>
<td>1.27</td>
<td>283</td>
<td>0.438</td>
<td>1.546</td>
<td>+1.02</td>
<td>+0.54</td>
<td>-0.30</td>
</tr>
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<td></td>
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<td>-14.09</td>
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<tr>
<td>1.34</td>
<td>244</td>
<td>0.462</td>
<td>1.333</td>
<td>+1.41</td>
<td>+1.16</td>
<td>+0.07</td>
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<td></td>
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<td>-15.01</td>
<td>-17.23</td>
<td>-17.54</td>
</tr>
<tr>
<td>1.42</td>
<td>193</td>
<td>0.49</td>
<td>1.055</td>
<td>+1.73</td>
<td>+2.02</td>
<td>+0.57</td>
</tr>
</tbody>
</table>
discrepancy. Pressures are not so good as for diatomics but the relative errors are misleadingly large because the simulations aimed for near zero pressures to allow comparison with experiment. For diatomics, it was the accuracy of the median approximation for higher pressures that was most impressive but, in the triatomic case, there are no high pressure simulations.

There are some molecular dynamics simulation results for thermodynamics of tetrahedral LJ models of CCl$_4$ [22] and CF$_4$ [23], obtained using the quaternion algorithm due to Evans [24], and also some Monte Carlo results for CCl$_4$ [25]. We find that the median-like methods fail completely for tetrahedral molecules in the region of available simulations. As an example of the least bad results, we quote those for a single state point of CCl$_4$ modeled with $l = 1.766$ Å, $\sigma_{CC} = 3.2$ Å, $\sigma_{CCI} = 3.5$ Å, $\varepsilon_{CC}/k_B = 51.2$ K, and $\varepsilon_{CCI}/k_B = 143.5$ K [22]. For $\rho \sigma_{CCI}^2 = 0.128$ and $k_B T/\varepsilon_{CCI} = 3.923$, the simulation gives $\rho \sigma_{CCI}^2/\varepsilon_{CCI} = 0.05$, $U/N \varepsilon_{CCI} = -11.48$ while the ESP of type (iii) gives $\rho \sigma_{CCI}^2/\varepsilon_{CCI} = 1.14$, $U/N \varepsilon_{CCI} = -2.83$. The ESP pressures become much worse still at lower temperatures. Despite the poor results, it is interesting to note that the two very different molecular potentials in [22] give very similar ESPs.

(b) Overlap potential

The overlap potential [26] is defined by

$$ v(R, \theta_1, \theta_2) = 4\varepsilon \left( \left( \frac{\sigma}{R} \right)^{12} - \left( \frac{\sigma}{R} \right)^{6} \right) + 8\delta \left( \frac{\sigma}{R} \right)^{12} F_0(\theta_1, \theta_2), $$

(11)

where $\theta_1, \theta_2$ are the polar angles of molecular axes relative to $\mathbf{R}$ and $P_2$ is the Legendre polynomial of order 2. It is a very simple way of crudely modelling the effect of the addition of short range anisotropy to a LJ atom. Our interest in it here is largely due to the fact that its median can be calculated analytically (see Appendix of [9]) and is just a LJ potential

$$ \nu(R) = 4\varepsilon \left( \left( \frac{\sigma}{R} \right)^{12} - \left( \frac{\sigma}{R} \right)^{6} \right), $$

(12)

where $\varepsilon' = K^{-1} \varepsilon$, $\sigma' = K^{1/6} \sigma$, $K = 1 - 2\delta(1 - 3/\pi)$. Consequently median thermodynamics can be found from the fitting functions of Nicolas et al. [27] or Ree [28] for the LJ fluid. We choose to use the latter fit and the results are compared to simulation results in figure 1 for various values of $\delta$ at a single density and temperature.

Clearly, for $\delta < 0$ (oblate) the median is worse than the mean (equivalent to $\delta = 0$). For $\delta > 0$ (prolate), the median is better than the mean but it is still not very accurate except at small $\delta$. The failure of the median ESP in the oblate case is a manifestation of a more general situation: Consider any potential of the form

$$ v(R, \Omega^a, \Omega^b) = s(R) + \delta F(\Omega^a, \Omega^b) R^{-\gamma} $$

(13)

and an angular average $\bar{v}(R)$ defined by

$$ \int d\Omega^a \int d\Omega^b f [v(R, \Omega^a, \Omega^b) - \bar{v}(R)] = 0, $$

(14)
Figure 1. Change of internal energy due to anisotropy for the overlap fluid at $\rho a^3 = 0.85$, $k_B T/\epsilon = 1.29$. $\bigcirc$, MD results of Haile quoted in [26]; ---, median results; ----, RAM results.

where $f$ is an arbitrary function. Then

$$\tilde{v}(R) = s(R) + \delta \tau R^{-\gamma},$$

(15)

where

$$\int d\Omega^a \int d\Omega^b f [F(\Omega^a, \Omega^b) - \tau] = 0.$$  

(16)

Provided $\tau \neq 0$ and $\delta$ can take either positive or negative values then, for $\delta \tau > 0$, $\tilde{v}(R) > s(R)$ for all $R$. However, when a spherical liquid has not too extreme an anisotropy added, the molecules will tend to reorient into lower energy configurations and so any ESP which gives the correct energy must have $\tilde{v}(R) < s(R)$ for at least some $R$.

We briefly digress here to point out that the (temperature dependent) RAM potential [29] $v_T(R)$, defined by

$$\int d\Omega^a \int d\Omega^b [\exp \{-\beta v(R, \Omega^a, \Omega^b)\} - \exp \{-\beta v_T(R)\}] = 0,$$

(17)

does not fall into the class of averages represented by equation (14). It is expected to give energy lowering for both positive and negative $\delta$ since the Boltzmann factor averaging always gives markedly greater weight to attractive potentials. For the overlap potential, we easily find that

$$v_T(R) = 4\varepsilon \left\{ \left( \frac{a}{R} \right)^{12} - \left( \frac{a}{R} \right)^6 - 2\delta \left( \frac{a}{R} \right)^{12} \right\} - \beta^{-1} \ln \left\{ \frac{J_2(\sqrt{\Lambda})}{\Lambda} \right\},$$

(18)
where
\[
\Lambda = 12 \beta \varepsilon_0 \delta \left( \frac{\sigma}{R} \right)^{12}, \quad J_0(x) = \int_0^x dt \exp \left\{ -(\text{sgn} \, \delta) t^2 \right\}.
\]

RAM internal energies have been calculated for the overlap potential using Ross' procedure [18] (taking care to allow correctly for the temperature dependence of the RAM potential) and are shown in figure 1. The internal energy is indeed lowered from its \( \delta = 0 \) value for both positive and negative values of \( \delta \), but the size of the effect is considerably overestimated for large \( |\delta| \).

For prolate overlap molecules, the median seems to provide a better reference system than the mean, but is not (in zero order) as accurate as for diatomics. In view of the simplicity of the potential this appears the most likely system to be amenable to perturbation expansion about the median reference system. In the usual spirit of perturbation theories about a spherical reference system we require that the first order term vanish. This is ensured by choosing the form of perturbation [12]
\[
\psi(R, \Omega) = (1 - \lambda^2)\psi(R) + k_5 T\lambda(1 - \lambda) \text{ sgn } [\psi(R, \Omega) - \psi(R)] + \lambda^2 \psi(R, \Omega).
\]

(19)

Then the hardest integral to evaluate in the second order term of the free energy expansion is proportional to
\[
\int d1 \int d2 \int d3 \, \gamma^\text{(a)}(1, 2, 3) \text{ sgn } [\psi(1, 2) - \psi(\mathbf{R}_{12})] \text{ sgn } [\psi(1, 3) - \psi(\mathbf{R}_{13})]
\]

(20)

where the superscript of the triplet distribution function indicates that it refers to the median potential. The angular part of the integral in (20) may be written
\[
\int_0^\pi d\phi \int_0^1 d\mu_1 \int_0^1 d\mu_2 \int_0^1 d\mu_3 \text{ sgn } \left( \mu_1^2 + \mu_2^2 - \frac{2}{\pi} \text{ sgn } \left( \mu_0^2 + \mu_3^2 - \frac{2}{\pi} \right) \right)
\]

(21)

where \( \mu_i = \cos \theta_i, (i = 1, 2, 3) \), \( \mu_0 = \cos \alpha \cos \theta_1 + \sin \theta_1 \cos \phi \), and \( \alpha \) is the angle between \( \mathbf{R}_{12} \) and \( \mathbf{R}_{13} \). (\( \phi \) represents the azimuthal angle for the axis of molecule 1 about \( \mathbf{R}_{12} \)).

It is elementary to reduce the expression (21) to
\[
\int_0^\pi d\phi \int_0^1 d\mu_1 \gamma \left( \frac{2}{\pi} - \mu_1^2 \right) \gamma \left( \frac{2}{\pi} - \mu_0^2 \right)
\]

(22)

where
\[
\gamma(x) = \begin{cases} 
1 & (x < 0) \\
1 - 2\sqrt{x} & (0 < x < 1)
\end{cases}
\]

(23)

but we are then left with a five-dimensional integral to evaluate numerically. Whilst this is certainly feasible it is equally certain not simple and is likely to consume considerable computer time, even when the commonly used Kirkwood superposition approximation is used for \( \gamma^\text{(a)}(1, 2, 3) \). The procedure of expansion in spherical harmonics which makes perturbation theory about the angular mean and RAM reference systems easily practicable [26, 29] does not appear promising.
for median perturbation theory due to the singular nature of the sgn function or
the function $\gamma$ arising from it. Thus we have not considered it worthwhile to carry
out numerical calculations of the above approximation even for this extremely
simple molecular model.

(c) Remark on multipolar potentials

For molecules where the only anisotropy is multipolar, the median potential is
not useful. Indeed for dipoles [17] and other odd multipoles the median is just
the isotropic part of the potential. We have remarked previously [14] that the
median potential for dipolar hard dumbbells is more repulsive than that for the
corresponding nonpolar dumbbells. More recently we have found that a similar
effect occurs when a dipole (ideal or otherwise) is added to a diatomic Lennard-
Jones molecule. Thus, the median has exactly the opposite effect to that necessary
to produce correct physical results for dipolar molecules with nonspherical repul-
sive cores. (Addition of a dipole moment should lower the internal energy.)

3. DISTRIBUTIONS OF POTENTIAL VALUES

A proper understanding of why the median potential yields such extremely
accurate thermodynamics in some cases is still lacking. The mystery is only
deepened by its failure for correlation functions [10, 11] and none of the mathe-
matical arguments in [7, 8, 15] give any clue as to why the median should give
much better thermodynamic results for linear triatomic than for tetrahedral mol-
ocules. Indeed, it is natural to think that, in at least one sense, tetrahedra are
'closer' to spherical symmetry than triatomics: in the large $R$ expansion of the
molecular potentials, the first angle dependent term occurs at a higher negative
power of $R$ for tetrahedra than for triatomics. Perhaps the best heuristic approach
is the use of frequency distributions for pair potential energy values at fixed

![Figure 2](image)

Figure 2. Frequency distribution of potential energy values at fixed centre–centre dis-
tance $R = 3l$ for the $r^{-12}$ term in $v_{st}$ of a linear triatomic. Both frequency and
potential energy units are arbitrary. The vertical line indicates the median of the
distribution.
The angular median and related potentials

Figure 3. As figure 2 for \( v_{YY} \) of a linear triatomic.

separation and all possible orientations, first introduced by Gray and Joslin [17]. Here we use this approach in an attempt to gain some insight into the results of the previous section.

Considering first polyatomic molecules, we show in figures 2–5 frequency distributions of the \( r^{-12} \) parts of the atom–atom potentials of linear triatomic and tetrahedral molecules. We see that the distributions for tetrahedral molecules lack the sharply peaked shape of those for linear triatomics. The value \( R/l = 3 \) chosen corresponds, for the triatomic \( v_{YY} \) (figure 3), to figure 5 of [14] where the frequency distribution was given for the full diatomic LJ potential. Comparison of these two figures shows the effect of the potential splitting: both distributions are highly peaked, but the median is quite close to the peak position only for the softer potential. It appears from these examples that the median method only

Figure 4. As figure 2 for \( v_{YY} \) of a tetrahedral molecule.
works well for anisotropic short-ranged repulsion when applied to a distribution of potential values that is strongly skewed towards low values and has a median close to a sharp peak.

We can also look at the above observations in a slightly different way. The usefulness of the median in statistical analysis is precisely the fact that it tends to ignore 'rare values'. For diatomic molecules of not too great elongation, the 'rare energies' are for end-to-end configurations and it is good to ignore these since they comprise the energetically unfavourable tail of the frequency distribution. For elongated diatomics, the crossed configurations become very energetically favourable compared to parallel and 'tee' ones [11], and therefore represent additional 'rare energies'. Ignoring these is a failing of the median but this is minimized by splitting the total potential into the least rapidly varying parts consistent with the molecular geometry [9].

For CCl₄, the important configurations are those where a Cl atom of one molecule fits between three Cl atoms of another molecule. These are presumably 'rare' compared to those configurations where a Cl atom of one molecule opposes one from the second molecule, this being reflected in the slow fall-off of the frequency distribution from its values at the lowest energies. We suspect therefore that the accurate validity of any ESP over a wide range of states is less likely than for diatomics, but presumably ESPs can be found entirely empirically which reproduce some range of experimental thermodynamic data for tetrahedral molecules.

Further insight may be obtained by considering the overlap potential. Here the frequency distribution is easily calculated analytically from

\[
p(F_0) \, dF_0 = \begin{cases} \frac{\pi}{6} dF_0 ; & -1 < F_0 < \frac{1}{2} \\ \left[ \frac{\pi}{6} - \frac{3}{4} \cos^{-1} \left( \frac{1}{2} \right) \right] dF_0 ; & \frac{1}{2} < F_0 < 2. \end{cases} \tag{24}
\]
\[\rho(F_0) \text{ is plotted in figure 6 and gives the shape of the potential value distribution for prolate overlap molecules. Compared to the mean, the median tends to ignore the tail of the distribution at high potential values and so the median results improve on those of the mean. However, since the distribution is not at all peaked, the median results are still poor. The distribution for oblate overlap molecules is just the opposite of that for the prolate case. The median now ignores the important contribution of the low energy tail of the distribution.}

Incidentally, frequency distributions of the potential indicate how poor a representation of real molecules the overlap potential is. Site–site models of prolate molecules, which have some potential values essentially arbitrarily large at small separations, seem much more realistic. The oblate overlap distribution correctly has a finite tail at low values but a real polyatomic oblate molecule (such as benzene) will clearly also have a few arbitrarily high potential values at small separations.

A large quadrupole moment is well known to have a significant effect on molecular thermodynamics. This is partly due to long range effects which the median obviously cannot be expected to describe accurately. The rather flat frequency distribution (figure 7) of a pure ideal quadrupole–quadrupole interaction potential

\[v(R, \theta_1, \theta_2, \phi_{12}) = \frac{Q^2}{R^6} F_Q(\theta_1, \theta_2, \phi_{12}),\]

\[F_Q(\theta_1, \theta_2, \phi_{12}) = \frac{3}{16}[1 - 5 \cos^2 \theta - 5 \cos^2 \theta_1 - 15 \cos^2 \theta \cos^2 \theta_2 \sin \theta_1 \sin \theta_2 \cos \phi_{12} - 4 \cos \theta \cos \theta_2 \cos \phi_{12} \sin^2 \theta_1 \sin^2 \theta_2],\]

shows, in the light of the above discussion, that the median method is also unlikely to be useful for treating the near neighbour effects in any strongly quadrupolar fluid. As for prolate overlap molecules, the median is slightly better than the mean but, because the distribution is not strongly peaked, not very accurate.
Based upon results reported here and in previous papers [14, 9, 12, 13] we conclude that median-like potentials are useful for predicting thermodynamics of prolate site-site molecules. The method's areas of success have been tentatively related to the shape of potential distributions at fixed $R$. It is successful when, for small $R$, there is a pronounced peak near the minimum energy including nearly half of all possible configurations. For larger $R$, the distribution is narrower and almost uniform so that the median is close to the mean. Oblate and nonlinear molecules do not have the required shape of distribution at small $R$ and the median is not successful for them; prolate overlap molecules represent another failure for the median but their rather pathological potential distribution (figure 6) seems to indicate that they form a very poor model of the anisotropic repulsion in real molecules. We seem thus to have delineated, albeit in an empirical manner, the limits of the usefulness of median-like potentials.

Finally we make a few more general remarks on sphericalized potentials. The advantage for large scale molecular thermodynamic calculations of an ESP over a spherical reference potential to be used in perturbation theory seems clear. The median potential itself is only suitable as an ESP for the limited range of molecular models indicated but differently defined ESPs may work for other types of potential. One possibility is the empirical $B_2$-inversion procedure of Smith and collaborators [30, 31] which has recently been formalized [32]. However, it is more suited to inversion of experimental thermophysical data, since calculation of $B_2(T)$ from a given nonspherical potential is itself a fairly major undertaking. Another spherical potential giving the exact $B_2(T)$ for a molecular potential (but avoiding its explicit evaluation) [33] has a cusp and so probably cannot be reliably treated by the standard methods for atomic fluids.
Due to lack of extensive simulation data for anything other than homonuclear nonpolar diatomics it is hard to judge whether useful ESPs exist for other molecular potential models, let alone give a prescription for obtaining them from a given model. For example, most simulation studies of multipoles to date have chosen a fixed state point and varied the multipole strength. A prerequisite for determining a suitable ESP (if such exists) will be simulation data for an extensive region of the temperature-density plane, fit only for a few specific molecules.

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*Note added in proof.*—The recently suggested variationally optimized ESP of Shaw *et al.* [34] leads to very accurate results for extremely elongated diatomics. For prolate molecules, however, their potential is just the median which as we have seen is not very accurate. For oblate overlap molecules, the variationally optimized potential is the midpoint of the range of the potential distribution; this is still given by equation (12) but with $K_{\delta} = 1 - |\delta|$. As a result, the energy is lowered compared to $\delta = 0$ but the overestimation of this effect is even greater than that predicted by the RAM potential.

**References**


[32] Maitland, G. C., Vesovic, V., and Wakeham, W. A., 1985, *Molec. Phys.*, **54**, 301. Equation (67) of this paper is in error; $\frac{1}{2}$ should be replaced by $\frac{1}{3}$. The corrected result is consistent with the general observation that the median is lower than the mean for prolate molecules.