

Equations of State of Nonspherical Fluids by Spherical Intermolecular Potentials

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Equations of state of nonspherical fluids by spherical intermolecular potentials

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The equilibrium properties of anisotropic molecular fluids can be in principle calculated in a statistical mechanics framework, but the theory is generally too cumbersome for many practical applications. Fortunately, at high densities and temperatures the anisotropy can be ‘averaged-out’ by means of a density and temperature independent potential (the ‘median’) that produces reliable thermodynamics [1,2].

The proposal of Shaw and Johnson [1], which turns out to be the so-called median potential [2], is very successful in predicting the thermodynamics of simple fluids such as N₂ and CO₂ at reasonable high pressures and temperatures [3]. Lebowitz and Percus [2] pointed out some time ago that the success of this approximation could perhaps be understood in terms of a simple theory that treats the asphericity as a perturbation. The median appears to be the best choice for hard nonspherical potential [4], which may explain its success for fluids at high densities, where the hard core contribution is known to be dominant.

For the more general case of a mixture the median is defined independent of density, temperature and concentrations for both like-pair and unlike-pair interactions by

$$\int \text{sgn}(\phi^{ab} - \phi_0^{ab}) d\Omega_1 d\Omega_2 = 0, \quad (1)$$

where ϕ^{ab} is the anisotropic potential and ϕ_0^{ab} is the sphericalized one for the interaction between the a and b components, and the integration is performed over the angular orientations of the two interacting molecules.

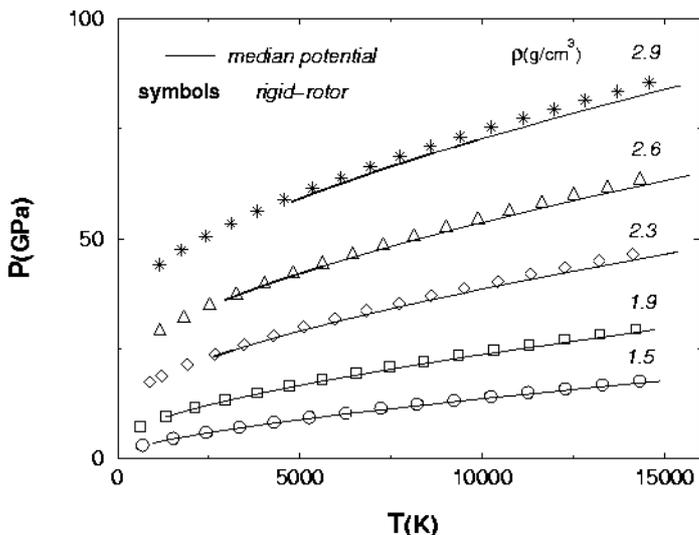


Fig. 1. Test of median potentials for an equimolar N₂ + O₂ mixture.

Anisotropic fluids such as N₂, O₂, CO₂ appear as detonation products at high pressures and temperatures, generally in mixed form. Therefore, we test the median prescription for equimolar mixtures of N₂ + O₂ and N₂ + CO₂, by comparing the results of MD simulations with rigid rotor atom-atom potentials and with sphericalized potentials in an extended range of densities and

temperatures. For the rigid rotor calculations we use *exp-6* potentials:

$$V(r) = \epsilon/(\alpha - 6)\{6 \exp[\alpha(1 - r/r^*)] - \alpha(r^*/r)^6\}. \quad (2)$$

The N-N and O-O parameters were extracted from Hugoniot data and for N-O we used the Lorentz-Berthelot rule.

We show in Fig. 1 the results of constant density simulations for the N₂ + O₂ mixture. The agreement between the rigid rotor and the median potential results is very good in a wide range of pressures and temperatures. For the N₂ + CO₂ mixture the agreement is limited to lower densities, largely because CO₂ is a stronger anisotropic molecule. We propose a heuristic method for improving the median recipe for such molecules by taking into account three-particle correlations.

Perhaps the greatest advantage of the median potential over other effective spherical potentials [6] is the fact that it is independent of density and temperature. The success of the median justifies in fact the analysis and interpretation of experimental shock-wave data on anisotropic fluids in terms of isotropic potentials. These potentials, generally obtained by fitting Hugoniot data [7], prove to be reliable in predicting thermodynamic properties at high pressures and temperatures [5].

Given the success of the median, in particular for molecules like N₂ and O₂, we believe that such potentials can be in fact treated like medians and inverted to yield atom-atom potentials. We carried out this task for N₂ and O₂ by assuming an *exp-6* form for the N-N and O-O interactions. This simple functional form turns out to be sufficient for extracting with very good accuracy atom-atom potentials from the N₂-N₂ and O₂-O₂ intermolecular interactions. The agreement between our O-O potential and an O-O potential used to model solid state data of molecular O₂ is very good, showing that unique sets of atom-atom potentials should perhaps be sufficient to describe the thermodynamic properties of simple anisotropic molecular systems in both fluid and solid states.

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