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Thermodynamics of anisotropic fluids using isotropic potentials

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We study the effectiveness and limitations of the median potential recipe for mixtures such as N₂ + O₂ and N₂ + CO₂, that are important in detonation applications. Conversely, we treat effective spherical potentials extracted from Hugoniot experiments (e.g., N₂ and O₂) as median potentials and invert them to extract atom-atom potentials. The resulting non-spherical potentials compare remarkably well with the atom-atom potentials used in studies of solid state properties. Finally, we propose a method to improve the median potential for stronger anisotropic fluids such as CO₂ and its mixtures.

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 spherical potential (the 'median') that produces reliable thermodynamic data [1,2].

Lebowitz and Percus [2] pointed out some time ago that the success of this approximation can perhaps be understood in terms of a simple theory that treats the asphericity as a perturbation. The idea can be summarized for the more general case of a binary mixture X + Y as follows: If φₐᵇ(r, Ω₁, Ω₂) is the anisotropic potential between molecules of type a and b (a and b run from 1 to 2, where 1 stands for X and 2 for Y) and φ₀ᵇ(r) the corresponding effective spherical potential, we write φₐᵇ(r, Ω₁, Ω₂) = φ₀ᵇ(r) + Δₐ[φₐᵇ, φ₀ᵇ], with 1 ≥ γ ≥ 0 and Δ₀[φₐᵇ, φ₀ᵇ] = 0, Δ₁[φₐᵇ, φ₀ᵇ] = φₐᵇ - φ₀ᵇ. Then, if we expand the Helmholtz free energy as

F = F₀ + γ(∂F/∂γ)|₀ + ...

the condition that the first order correction is zero, (∂F/∂γ)|₀ = 0, imposes a restriction on the potentials φₐᵇ(r). If the concentrations of the X and Y molecules are x and y (x + y = 1), this translates into

½x²∫ g₀ₓₓ(r₁, r₂)(∂Δₓₓ X/∂x)|₀dr₁dr₂dΩ₁dΩ₂ + xy∫ g₀ₓᵧ(r₁, r₂)(∂Δₓᵧ/∂x)|₀dr₁dr₂dΩ₁dΩ₂ + ½y²∫ g₀ᵧᵧ(r₁, r₂)(∂Δᵧᵧ Y/∂y)|₀dr₁dr₂dΩ₁dΩ₂ = 0

where g₀ᵦ are the pair correlation functions for the sphericalized system. The above condition can be enforced independently of density, temperature and concentrations if we require ∫(∂Δᵦᵦ/∂x)|₀dΩ₁dΩ₂ = 0 for all a's and b's. The form of the effective spherical potentials, for both like-pair and unlike-pair interactions, depends of course crucially on our choice for Δᵦᵦ (in fact only ∂Δᵦᵦ/∂x)|₀, which unfortunately is left undefined by the perturbation expansion.

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 reasonably high pressures and temperatures [3,4]. The median is defined by using ∂Δᵦᵦ/∂x)|₀ = sgn(φₐᵇ - φ₀ᵇ), and appears to be the best choice for hard nonspherical potentials [5]. This may explain its success for fluids at high densities, where the hard core contribution is known to be dominant.

Anisotropic fluids such as N₂, O₂, CO₂ appear as detonation products at high densities and temperatures, generally in mixed form [6]. Therefore, we test the median potential 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 atom-atom exp - 6 potentials,

V(r) = c/(α - 6)(6exp[α(1 - r/r*)] - α(r*/r)⁶)

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

The N₂ and O₂ molecules are moderately anisotropic, with bond lengths l₀ₙ₂ = 1.098Å, l₀ₒ₂ = 1.207Å, and rₙ₂/l₀ₙ₂ ≈ 0.29, rₒ₂/lₒ₂ ≈ 0.35. 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 the range of densities and temperatures studied. This is probably not entirely unexpected as N$_2$ is a good candidate for spher- icalization [3], while O$_2$ is only slightly more anisotropic, as shown by its $r^* / l$ ratio.

To study the N$_2$ + CO$_2$ mixture we used a simplified model for the CO$_2$ molecule [4], that only takes into account the oxygens as centers of force. While this model may not be an accurate predictor of experimental data, it does reproduce the basic anisotropy of the CO$_2$. The length of the CO$_2$ molecule is $l_{CO_2} = 2.32\text{Å}$, and $r^* / l_{CO_2} \approx 0.70$, which makes it much more anisotropic than either N$_2$ or O$_2$. The agreement between the rigid rotor and the sphericalized potential results is limited to smaller particle densities than in the case of N$_2$ + O$_2$. (Note that a density of 2.3g/cm$^3$ for N$_2$ + CO$_2$ yields approximately the same particle density as 1.9g/cm$^3$ in the case of N$_2$ + O$_2$.)

Perhaps the greatest advantage of the median potential over other effective spherical potentials [7] is the fact that it is independent of density and temperature. The success of the median recipe 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 [8-11], prove to be reliable in predicting thermodynamic properties at high pressures and temperatures [6].

Given the success of the median, in particular for molecules like N$_2$ and O$_2$, we therefore believe that such potentials can be treated like medians and inverted to yield atom-atom potentials. We carried out this task for N$_2$ and O$_2$, 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 N$_2$ - N$_2$ and O$_2$ - O$_2$ intermolecular interactions. We show in Fig. 2 our O - O potential, together with an O - O potential used to model solid state data of molecular O$_2$ at high pressures [12]. The agreement 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.

The lower accuracy of the median for N$_2$ + CO$_2$ mixtures, in particular at higher temperatures, can be largely traced back to its performance in the case of pure CO$_2$. - see Fig. 3. Nevertheless, given the general success of the median prescription, we would like to improve it in a systematic way. Unfortunately, the basis for the median construction is rather heuristic [2,5], and seems to defy a full explanation [13,14].

To make progress, we turn to the observation that the
median minimizes the sum of absolute deviations \[\int d\Omega_1 \int d\Omega_2 |\phi(r, \Omega_1, \Omega_2) - \phi_0(r)|.\] We interpret this as an effective way of constructing an isotropic interaction between two isolated molecules.

However, at high densities, in particular for hard bodies, the presence of a third molecule will restrict the configurations available to the first two molecules. We take this into account in an heuristic way by using a relatively small number of positions for the third molecule; details will be reported elsewhere [16]. The new potential, that we call corrected median, yields results as shown in Fig. 3. We believe that they are promising, as they improve the pressure predictions, in particular at high temperatures. Further refinements and the testing of the procedure for mixtures are underway [16].

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