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DENSE MOLECULAR THERMODYNAMICS

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We are examining the thermodynamics of dense molecular fluids from the theoretical view. Our interests range from modeling single-species, spherically symmetric, atomic systems, through adding the complication of nonspherical molecular potentials, to mixing various molecular species with the inclusion of chemistry. We discuss what has been accomplished and evaluate the directions to be taken in attacking the unsolved problems. The various theoretical approaches, both analytic and numerical, are presented. We finish with a discussion of the recent advance in treating nonspherical molecular potentials with effective spherical potentials in the calculation of thermodynamics.

We are interested in understanding and modeling the thermodynamics of dense, hot molecular fluids. Our attention is centered on those fluids that are produced behind detonation fronts propagating through high explosives. Thus the regime is that of densities 2-3 times normal liquid densities, temperatures of 1 to 6 kK, and pressures of 100-400 kbar. A prototypical system is a mixture of N_2 , CO_2 , H_2O , and carbon. We, of course, go outside this regime to test our methods, and we look to simpler systems to develop our ideas.

Our attack can be divided into three fundamental problems. The first want to understand single-species fluids with spherically symmetric potentials (atomic fluids). Through decades of effort by many researchers, this problem has been solved by any of several hard-sphere perturbation theories.¹ Because of its ease of application and its accuracy, our favorite variety is the variational hard-sphere theory of Mansoori and Canfield and Ross² as modified by Ross.³

The second question to be addressed is the calculation of the thermodynamics for real molecular fluids without spherical symmetry. In the literature there exists a number of methods, from theories such as RISM⁴ that are too complex and, for our regime, of questionable accuracy, to simpler approaches that attempt to find effective spherical potentials⁵ that model the thermodynamics of the true anisotropic potentials. Because they are simple, we favor the latter, but our intuition as to which of the many angular averaging schemes is accurate had to be developed. We will discuss in greater detail the question in the last part of this paper.

Finally, the true detonation product fluids are mixtures of many molecular species with chemistry occurring. Thus it is imperative that an efficient and accurate mixing procedure be determined. The existing literature has three candidates: ideal mixing, the various forms of

van der Waals mixing, and hard-sphere perturbation theory using a mixture of varying diameter hard spheres.⁶ The last approach is probably too complex for practical calculations. The first two are promising, but more investigations into their accuracy are desirable.

In limiting ourselves to the above questions, we have swept under the carpet at least three interesting and important problems. In our thinking, we have separated out the electronic degrees of freedom and treated them, except for minor modifications, as in an ideal gas. The chemistry, in particular how dissociation energies are used, has similar approximations. The vibrational modes are also separated as for an ideal gas. Because so many ideal gas concepts are implicit in these treatments, there are worries as to their validity for the densities of interest. A pet question wonders about qualitative changes in electron screening and correlation energies. We have performed one minor study of tightly bound vibrators and find no problem in applying the simple vibrational model, but this is a minor, inconclusive test. Experimental data and better theory are needed to find the density dependence of electronic levels, vibrational levels, and dissociation energies at the high densities of interest.

We will now illustrate the approach taken in developing and testing the approximate analytic theories used in dense fluid theory. This consists of an interplay between the approximate models being formulated and essentially exact, within the framework of a given molecular or atomic potential, numerical work. By using molecular dynamics (MD), one produces the thermodynamic and finer details of an equilibrium system that have only controlled numerical and statistical errors and that can be used to refine and evaluate the approximate, but much more easily applied, analytical models. (The MD, while accurate, is very time consuming and expensive.) The analytic models greatly aid in the interpretation of the MD.

We use this above approach in the development of a new, highly accurate, sphericalization procedure for molecules (SPM)⁸ that can be viewed in two ways. If one is working from a given nonspherical potential, SPM simply provides an effective spherical potential that, when used with the existing hard-sphere perturbation theory, models very accurately, the true thermodynamics. Alternatively, SPM justifies the established procedure of fitting experimental shock data with a spherical potential and extrapolating off the Hugoniot. We look at how we develop SPM and how well it performs. We just need the baseline data of MD and thus a good potential for some test system, in our case N_2 .

We treat the molecular potential as a sum of the atomic interactions (an atom-atom potential) with the bond distance allowed as a free parameter. Our analytic form for the atom-atom potential is an exp-6 or Buckingham potential.¹⁰ Colleagues at Los Alamos furnished us with theoretical configuration-interaction (CI), electron gas (EG), and perturbation (MBPT) calculations of the N_2 - N_2 potential as a function of center-of-mass separation for various orientations.¹¹ We fit to their CI and EG numbers with the very good agreement shown in Fig. 1. We then use MD to compute for this molecular potential the Hugoniot curve shown as a coarse dashed line in Fig. 2. This is above the data by about 1-2 standard deviations. A 0.8 scaling of our initial fit potential results in a excellent fit given by the solid lines of Figs. 2 and 3. (The break in the data of Fig. 2 is probably due to dissociation of the N_2 molecule, physics not included in our modeling.) The MBPT shows that the 0.8 scaling is probably explained by the CI not being converged at the

Figure 1: Comparison of fit (solid lines) to quantum chemistry calculations (discrete symbols) of N_2 - N_2 potential. Four N_2 - N_2 configurations, X, PA, PB, and L, are shown.

Figure 2: N_2 Hugoniot data¹² (discrete symbols) compared to theory. Coarse dashed line uses the original fit shown in Fig. 1 while solid line represents the 0.8 scaling. Ignore the fine dashed line.

Figure 3: N_2 Hugoniot data¹² (triples of pluses with uncertainty given by vertical extent) compared to theory. Diamonds are from MD with the solid curve giving a fit to the diamonds.

lower energies of the potential and by many-body effects at the higher energies.

With our potential established, we use MD to produce the full equation of state (EOS). (We will give only the results for pressures. All we say for pressures applies for internal energies also.) Figure 4 presents as discrete symbols the MD EOS and Hugoniot. We then, as an empirical exercise, choose a spherical potential for the N_2 molecule of the exp-6 form. We adjust the potential parameters to fit the Hugoniot temperatures, pressures, and internal energies as a function of density. We, of course, add an explicit classical rotor term. (Note that it is not at all obvious that a

simultaneously good fit to all three Hugoniot functions is possible.) The result is indistinguishable from the solid curve of Fig. 3 and is the solid Hugoniot curve of Fig. 4, all in excellent agreement. The extrapolation off the Hugoniot with the effective spherical potential is shown in Fig. 4 by the solid line isotherms. The errors are less than 1.5% from the EOS of the true anisotropic potential. This establishes the existence of an accurate spherical averaging procedure for the thermodynamics of molecular systems, with the direct relation between the true and effective potentials, not yet defined.

One should worry that the physics responsible for the effectiveness of the spherical potential is trivial. Such a case would hold if the temperatures are high enough that an arithmetic average over angles is accurate. However, the high-temperature average produces a potential that is 35% too large. Another existing (initially our choice as the best) procedure is that of Perram and White¹³ where the effective potential ϕ is temperature dependent and given by

$$\hat{\phi} = -kT \ln \langle \exp(-\phi/kT) \rangle \quad (1)$$

$\langle \dots \rangle$ denotes angular average. However, again this is less than satisfactory. Figure 5 shows the comparison of the true EOS with that given by this average. If simple physics is responsible for the success of our effective spherical potential, it would seem that these other spherical potentials would be equally good; they are not.

Figure 4: Comparison of true N_2 EOS (discrete symbols) with that of empirical spherical potential (solid curves). Ignore the dashed curve.

Figure 5: Comparison of true N_2 EOS (discrete symbols) and Perram and White spherical theory (curves).

We do not have an understanding of the physical processes responsible for the accuracy of our effective potential. We do have an interpretation of the potential in terms of a particular angular average of the true anisotropic potential. The following analytic work guides us.¹⁴ We follow the research of Smith and coworkers¹⁴ and Shaw et al.⁸

We start by expanding the true Helmholtz free energy for the molecular potential ϕ_1 in a perturbation expansion around an arbitrary spherical potential ϕ_0 .

$$A_1 = A_0 + A_0^{(1)} + \frac{1}{2} A_0^{(2)} + \dots \quad (2)$$

To calculate $A_0^{(n)}$, we define an interpolation between ϕ_0 and ϕ_1 by

$$S[B(\phi_\lambda - \phi_0)] = \lambda S[B(\phi_1 - \phi_0)] \quad , \quad 0 \leq \lambda \leq 1 \quad (3)$$

ϕ_λ is the interpolating potential, B is a parameter that we will take to be large, and S is some invertible function. The $A_0^{(n)}$ are then $A_0^{(n)} = \partial^n A_0 / \partial \lambda^n |_{\lambda=0}$. By choosing S odd, roughly speaking, half of all terms in the infinite series, Eq. (2), are set to zero. With ϕ_0 satisfying

$$\langle S[B(\phi_1 - \phi_0)] \rangle = 0 \quad (4)$$

$A_0^{(1)}$ is zero. With B large and with reasonable choices of S , Ref. 8 shows that the other $A_0^{(n)}$ are small. Thus Eq. (4) with B large would appear to select a ϕ_0 such that A_0 is a good approximation to A_1 . A good choice for S is $\sinh^{-1}$. If $B \rightarrow \infty$, then $S[BX] \rightarrow \text{sign}(X)$ and ϕ_0 becomes the median of ϕ_1 . (The sign function selects the sign of X .)

Now how does our empirically determined spherical potential compare to the median of the anisotropic N_2 potential? To numerical accuracy they are the same. Both produce EOS's that agree with the MD to 1.5%. Our empirical potential can therefore be interpreted as the median.

We have compared the true N_2 second virial coefficient to that produced by the median. The agreement is good, with 6% differences typical. We use the N_2 MD data of Cheung and Powles¹⁵ to test the median near the triple point. The internal energies agree to 2% while pressures are somewhat disappointing. However, in the triple point region, the pressure is very sensitive to small changes in the potential. It appears that the median potential is within 2-4% of a potential that would accurately reproduce the true pressure.

Therefore, for N_2 we have learned that a median of the true molecular potential does very well in producing the true thermodynamics, especially in high density fluids. We have preliminary results for CO_2 at high density that indicates that the median gives 3% results. We feel that SPM is valid for the thermodynamics of physically realistic potentials with the systems away from orientational phase transitions.

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