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Some Aspects of Equations of State

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Some Aspects of Equations of State

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SOME ASPECTS OF EQUATIONS OF STATE

by

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ABSTRACT

We develop briefly some elementary properties of the equation of state of molecules repulsing each other as point centers of force. An inequality for the Lennard-Jones gas is presented. We also briefly review the scaled particle theory equation of state of hard spheres. We suggest means of possibly applying these concepts to represent thermodynamic data on model detonating gases.

I. INTRODUCTION

During my recent visit to the Los Alamos Scientific Laboratory (LASL), John Bdzil asked me to make some remarks about some elementary approaches to equations of state of detonating gases. This report is a summary of some simple ideas drawn from elementary statistical mechanics. For our purposes, the gases we shall be concerned about are single fluids (or certain simple mixtures of fluids) at sufficiently high temperature and pressure so that the effective intermolecular potential is purely repulsive.

Two directions for doing this are to assume that at sufficiently high temperatures the real gas intermolecular potential can be replaced by either (1) point centers that repulse each other with the $(n+1)^{st}$ power of the distance between them, r, viz.,

$$\phi = A/r^n \quad , \tag{1.1}$$

$\phi = \phi(r)$ being the effective intermolecular potential; or (2) the molecules act as hard spheres with a diameter σ. The latter can be made to depend weakly on the temperature T.

The first approach is simple because it enables one to deduce certain aspects of the mathematical form of the equation of state, even though the precise functional form is not determined by elementary considerations. Specifically, one can use thermodynamic scaling to obtain a relation between the pressure p, volume v, and internal energy U of such a gas. This result can be extended to mixtures of point centers of such form, e.g., for a binary mixture to a gas composed of N_1, molecules of type 1 and N_2 molecules of type 2, whose pairwise additive effective potentials are

$$\phi_{11} = A_{11}/r^n \quad , \quad \phi_{12} = A_{12}/r^n \quad , \quad \phi_{22} = A_{22}/r^n \quad .$$

This p,v,U relation can be used to obtain a possibly effective approximate way of extending empirical information at a reference temperature $T = T_r$ if $p_r = H(v_r)$ is found experimentally and one is morally certain that in the vicinity of $T = T_r$ the real gas satisfies Eq. (1.1). The success of this approximate procedure must of course be checked experimentally. In conjunction with this procedure, or alternatively, one can develop the thermodynamics of the gas on the basis of the given p,v,U relation. In this fashion one can generate some relationships which, while clearly exact for the presumed model, can be used to check the behavior of the real gas. We shall, in this report, carry out a portion of this program for a single-fluid gas. The thermodynamics of such a mixture we leave as an exercise for our readers.

In the second approach, where one models the gas molecules by hard spheres, one is using well-known results on hard-sphere equations of state generated from the scaled particle theory or solutions of the Percus-Yevick integral equation and certain empirical extensions. Much of modern, high-temperature statistical mechanical perturbation theory begins with this reference state! We shall propose a much more empirical set of approximations.

II. THE FLUID OF REPULSIVE POINT CENTERS ($\phi = A/r^n$)

We prefer to deduce the basic p,v,U relation from the canonical ensemble virial equation of state and internal energy representation.[1]

$$pv = NkT - \frac{2\pi N^2}{3v}\int_0^\infty \frac{d\phi(r)}{dr}\, g(r)r^3 dr, \tag{2.1}$$

$$U = \frac{3}{2}NkT + \frac{2\pi N^2}{v}\int_0^\infty \phi(r)g(r)r^2 dr \tag{2.2}$$

with N the number of molecules; k, Boltzmann's constant; $\phi(r)$, the intermolecular potential; and $g(r) = g(r, N/v, T)$ the radial distribution function. For Eq. (1.1)

$$\frac{d\phi}{dr} = -\, n\phi/r \tag{2.3}$$

and thus Eq. (2.1) and Eq. (2.2) become

$$\begin{aligned} (pv - NkT) &= \left(\frac{n}{3}\right)\left[\frac{2\pi N^2}{v}\int_0^\infty \frac{A}{r^n}\, g(r)r^2 dr\right] \;, \\ \left(U - \frac{3}{2}NkT\right) &= \left[\frac{2\pi N^2}{v}\int_0^\infty \frac{A}{r^n}\, g(r)r^2 dr\right] \;. \end{aligned} \tag{2.4}$$

Elimination of the joint factor in square brackets on the right-hand side of Eq. (2.14) yields the desired p,v,U relation

$$pv - \left(1 - \frac{n}{2}\right)NkT = \left(\frac{n}{3}\right)U \tag{2.5}$$

or

$$pv - \left(1 - \frac{3}{2}h\right)NkT = hU \;, \tag{2.6}$$

where the constant number $h = n/3$. We have written Eq. (2.6) to show the similarity to the often-used equation of state of solids[2]

$$pv - R(v,T) = hU \quad , \tag{2.7}$$

but for solids, R is a weak function of T whereas our R is independent of v.

Equation (2.5) also holds for the mixture of such point centers satisfying Eq. (1.2). For a binary mixture, Eq. (2.1) and Eq. (2.2) become

$$pv = (N_1 + N_2)kT - \frac{2\pi}{3v}\left[N_1^2 \int_0^\infty \frac{d\phi_{11}}{dr} g_{11}(r)r^3dr + 2N_1N_2\int_0^\infty \frac{d\phi_{12}}{dr} g_{12}(r)r^3dr + N_2^2 \int_0^\infty \frac{d\phi_{22}}{dr} g_{22}(r)r^3dr\right] ,$$

$$U = \frac{3}{2}(N_1 + N_2)kT + \frac{2\pi}{v}\left[N_1^2 \int_0^\infty \phi_{11}(r)g_{11}(r)r^2dr + 2N_1N_2 \int_0^\infty \phi_{12}(r)g_{12}(r)r^2dr + N_2^2 \int_0^\infty \phi_{22}(r)g_{22}(r)r^2dr\right] .$$

Substitution of Eq. (1.2) into the above and elimination of the joint factor

$$\left[N_1^2A_{11} \int_0^\infty r^{-n}g_{11}(r)r^2dr + 2N_1N_2A_{12} \int_0^\infty r^{-n}g_{12}(r)r^2dr + N_2^2A_{22} \int_0^\infty r^{-n}g_{22}(r)r^2dr\right]$$

yields Eq. (2.5) with $N = N_1 + N_2$. Of course the thermodynamics of such a multicomponent mixture are somewhat different from the pure fluid; nonetheless, many of our subsequent thermodynamic derivations can be extended to such a mixture with some modification. In the remainder of this section we focus only on the single-fluid gas.

Our result is a special case of a scaling, i.e., similarity argument given in detail in Landau and Lifshitz[3]. If the potential energy of interaction between the particles in a body are a homogeneous function of degree n in their coordinates, then the Helmholtz free energy, F, can be written in the form

$$F = - 3(1/2 + \frac{1}{n})NkT \ln(kT) + NkT\,\Psi(vT^{-3/n}/N) \quad , \tag{2.8}$$

where Ψ is an unknown function of the indicated argument. This result is obtained by considering the effect of the substitutions on the coordinates q and their conjugate moments $p(q \rightarrow \lambda q,\ p \rightarrow \lambda^{n/2}p)$, λ is an arbitrary constant, if we also substitute $v \rightarrow \lambda^3 v$ and $T \rightarrow \lambda^n T$ in the canonical partition function. p can be obtained by differentiating Eq. (2.8) or directly from the virial theorem. In our case, $n \rightarrow -n$ and Eq. (2.5) results. This argument can be extended usefully to the grand canonical partition function for mixtures satisfying Eq. (1.2), but we leave this as an excercise for our readers.

We now return to our single-fluid equation of state Eq. (2.6). Combining Eq. (2.6) with the thermodynamic relation

$$\left(\frac{\partial U}{\partial v}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_v - p \tag{2.9}$$

allows us to eliminate either U or p. Let us first do the former. Differentiating Eq. (2.6) with respect to v at constant T, one finds

$$h\left(\frac{\partial U}{\partial v}\right)_T = p + v\left(\frac{\partial p}{\partial v}\right)_T = h\left[T\left(\frac{\partial p}{\partial T}\right)_v - p\right]$$

by virture of Eq. (2.9). This can be rearranged to give

$$v\left(\frac{\partial p}{\partial v}\right)_T - hT\left(\frac{\partial p}{\partial T}\right)_v = - (1 + h)p \quad . \tag{2.10}$$

The characteristics of this partial differential equation (PDE) satisfy

$$\frac{dv}{v} = -\frac{dT}{hT} = -\frac{dp}{(1+h)p}$$

whose solutions are the characteristics

$$Tv^h = C_1 \equiv z$$
$$pv^{(h+1)} = C_2 \quad . \tag{2.11}$$

The general solution of Eq. (2.10) can therefore be written [cf. Eq. (2.8) with n → -n]

$$p = v^{-(h+1)}\ W(Tv^h) \quad , \tag{2.12}$$

where W is an unspecified function of the indicated argument.

Let us now show how this can be used to extend empirical data approximately. Suppose at the reference temperature $T = T_r$ one obtains experimentally the empirical relation

$$p_r = H(v_r) \quad . \tag{2.13}$$

Then if the characteristics are to pass through this curve in the $T = T_r$ plane, we must have from Eq. (2.11)

$$Tv^h = z_r = T_r v_r^h$$
$$pv^{(h+1)} = p_r v_r^{(h+1)} = v_r^{(h+1)}\ H(v_r) \quad ,$$

or

$$p = (T/T_r)^{\frac{h+1}{h}}\ H\left(v(\frac{T}{Tr})^{\frac{1}{h}}\right) \tag{2.14}$$

must be the equation of state in the vicinity of $T = T_r$.

Perhaps a larger range of validity of such an empirical representation can be achieved by allowing h to vary slightly with $T-T_r$ and $v-v_r$, viz.,

$$h = h_r + h_v(v - v_r) + h_T(T - T_r) \quad . \tag{2.15}$$

Clearly, by introducing enough parameters such as h_r, h_v, h_T, one should be able to fit just about anything in the way of p-v-T data, with consequent loss of meaning!

For the purposes of doing thermodynamics it might be useful to eliminate p from Eq. (2.9) using Eq. (2.6). One finds the PDE.

$$U = T\left(\frac{\partial U}{\partial T}\right)_v - h^{-1}v\left(\frac{\partial U}{\partial v}\right)_T \quad , \tag{2.16}$$

whose general solution is

$$U = v^{-h}f(z) \quad , \quad z = Tv^h \quad , \tag{2.17}$$

and f is undetermined. The functions f and W are of course related as is verified easily by substituting Eq. (2.17) and Eq. (2.12) into Eq. (2.6), which allows one to conclude that

$$W(z) = hf(z) + (1 - \tfrac{3}{2}h)Nkz \quad , \quad z = Tv^h \quad . \tag{2.18}$$

The physical significance of the function f(z) follows immediately from differentiation of U with respect to T at constant v,

$$C_v(z) = \left(\frac{\partial U}{\partial T}\right)_v = f'(z) \quad , \tag{2.19}$$

i.e., $f'(z)$ is the specific heat at constant volume. $f(z)$ also can be related easily to ψ of Eq. (2.8) by differentiating the latter.

We will not pursue the systematic thermodynamics of this gas but list only three parameters that might be of interest in detonation physics.

$(v \equiv \frac{hU}{p} + (1 - \frac{3}{2}h)\frac{NkT}{p};\ f'(z) = C_v;\ z = Tv^h)$

$$\alpha_p = \frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_p = \tag{2.20}$$

$$\frac{f'(z) + \left(\frac{1}{h} - \frac{3}{2}\right)Nk}{(h+1)U + \left(\frac{1}{h} - \frac{3}{2}\right)NkT - hTf'(z)} \quad ,$$

$$B_T = K_T^{-1} = - v\left(\frac{\partial p}{\partial v}\right)_T = \tag{2.21}$$

$$\frac{h}{v}\left[(h+1)U + \left(\frac{1}{h} - \frac{3}{2}\right)NkT - hTf'(z)\right] \quad ,$$

$$\Gamma = \text{Grüneisen ratio} = \frac{\alpha_p v}{K_T C_v}$$

$$= h\left[1 + \left(\frac{1}{h} - \frac{3}{2}\right)\frac{Nk}{f'(z)}\right] \quad . \tag{2.22}$$

Some final remarks about this excercise are

(1) One can redo easily everything if the gas has separable, internal degrees of freedom by noting that one only has to add a temperature-dependent contribution to U and proceed to redo the theory including that term.

(2) Clearly this gas reminds one of an ideal quantum gas in its thermodynamic properties. Specifically if $h = 2/3$ (hypothetical $n = 2$), then the thermodynamics becomes isomorphous with a fermion gas.

(3) One can also ask what happens to the p-v-U equation of state if the potential is no longer in the form of Eq. (1.1) but is, say, of the Lennard-Jones form

$$\phi(r) = A_n r^{-n} - A_m r^{-m} \quad , \tag{2.23}$$

where $n > m > 0$.

Remembering that $4\pi r^2 g(r)dr$ is the marginal probability distribution of pairs of molecules in a canonical ensemble and providing

$$\langle r^k \rangle = \int_0^\infty r^k g(r)\, 4\pi r^2 dr < \infty \quad , \tag{2.24}$$

$k = n,m$, we can show that Eq. (2.6) is now replaced by an inequality. Let

$$\omega_p = \frac{(pv/NkT) - 1}{\frac{N}{6vkT}} \quad ,$$

and

$$\omega_u = \frac{(U/NkT) - 3/2}{\frac{N}{2vkT}} \quad . \tag{2.25}$$

Then by virtue of Eq. (2.23) in Eq. (2.1) and Eq. (2.2) we have

$$\begin{aligned} \omega_p &= nA_n \langle r^{-n}\rangle - mA_m \langle r^{-m}\rangle \quad , \\ \omega_u &= A_n \langle r^{-n}\rangle - A_m \langle r^{-m}\rangle \quad . \end{aligned} \tag{2.26}$$

Solving for $\langle r^{-n}\rangle$ and $\langle r^{-m}\rangle$, one has

$$\begin{aligned} \langle r^{-n}\rangle &= \frac{\omega_p - m\omega_u}{(n-m)\, A_n} \quad , \\ \langle r^{-m}\rangle &= \frac{\omega_p - n\omega_u}{(n-m)\, A_m} \quad . \end{aligned} \tag{2.27}$$

Treating 1/r as a random variable one has, using standard inequalities on expectation values of convex functions of random variables,[4]

$$\left[\langle r^{-n}\rangle\right]^{1/n} \geq \left[\langle r^{-m}\rangle\right]^{1/m}$$

or

$$\left[\frac{\omega_p - n\omega_u}{(n-m)\, A_m}\right]^{1/m} \leq \left[\frac{\omega_p - m\omega_u}{(n-m)\, A_n}\right]^{1/n} \quad . \tag{2.28}$$

III. THE HARD-SPHERE FLUID

The principal characteristic of a fluid of elastic bodies, such as a hard-sphere fluid, is that the total pressure consists of the thermal pressure

$$p = T\left(\frac{\partial p}{\partial T}\right)_v \quad , \tag{3.1}$$

i.e., $(\partial U/\partial v)_T = 0$.
For such a fluid

$$\frac{Pv}{NkT} = 1 + \frac{2}{3}\pi\sigma^3\left(\frac{N}{v}\right) g\left(\sigma\left(\frac{N}{v}\right)^{1/3}\right) \quad , \tag{3.2}$$

where σ is the diameter of the sphere and $g(\sigma(\frac{N}{v})^{1/3})$ is the radial distribution function at contact. It can be shown that

$$B_T = - v\left(\frac{\partial p}{\partial v}\right)_T = \frac{p}{T\alpha_p} \quad , \tag{3.3}$$

$\alpha_p = v^{-1}(\partial v/\partial T)_p$. The Gruneisen ratio of such a fluid is given by

$$\Gamma = pv/TC_v \quad . \tag{3.4}$$

All of these are possible diagnostics for testing whether a real fluid behaves like a hard-sphere fluid.

The scaled particle theory (SPT) of fluids or the Percus-Yevick (PY) compressibility equation of state provides an approximate equation of state

$$\frac{pv}{NkT} = \frac{1 + \eta + \eta^2}{(1 - \eta)^3} \quad , \tag{3.5}$$

with $\eta = \rho\pi\sigma^3/6$, $\rho = N/v$. The quantities α_p and $B_T^{-1} = K_T$ are given in this theory by

$$\alpha_p = \frac{1 - \eta^3}{T(1 + 2\eta)^2} \tag{3.6}$$

$$K_T = \frac{\pi\sigma^3}{6kT} \frac{(1 - \eta)^4}{\eta(1 + 2\eta)^2} \quad . \tag{3.7}$$

Of course, Grüneisen's ratio satisfies Eq. (3.4).

I recommend that in using these relations the following procedure be followed for liquids.

(1) Use the empirical real fluid ρ, $\rho^{\text{exp.}}$.

(2) Find an appropriate $\sigma = \sigma(T)$ by using Eq. (3.7) to fit empirical data, i.e., solve for $\sigma(T)$ from Eq. (3.7) expressed as

$$K_T^{\text{exp.}} = \frac{\pi\sigma^3}{6kT} \frac{\left(1 - \frac{\pi\rho^{\text{exp.}}\sigma^3}{6}\right)^4}{\left(\frac{\pi\rho^{\text{exp.}}\sigma^3}{6}\right)\left(1 + \frac{2\pi\rho^{\text{exp.}}\sigma^3}{6}\right)^2} .$$

(3) Use this σ to find η for use in Eq. (3.5) and Eq. (3.6) and other thermodynamic relations that can be computed from these. (There is really no reason to believe that the Lennard-Jones σ parameters ought to apply in this theory with any accuracy.) One could also construct a procedure for detonating gases. We have not done so in this report.

For hard-sphere mixtures, one has the SPT result

$$\frac{p}{\rho kT} = \frac{1 + \xi + \xi^2}{(1 - \xi)^3} - \frac{\pi \rho}{2(1 - \rho)^3} \sum_{i < j = 1}^{m} x_i x_j (\sigma_{ii} - \sigma_{jj})^2 [2\sigma_{ij} + \sigma_{ii}\sigma_{jj} X] \tag{3.8}$$

with σ_{ii} the diameter of species i

$$\xi = \frac{\pi}{6}\rho \sum_{k=1}^{m} x_k \sigma_{kk}^3 ,$$

$$X = \frac{\pi}{6}\rho \sum_{k=1}^{m} x_k \sigma_{kk}^2 ,$$

$$\sigma_{ij} = \frac{1}{2}(\sigma_{ii} + \sigma_{jj}) ,$$

$$x_i = N_i/N .$$

For a binary mixture of large and very, very small hard spheres, one has the exact limiting relation[1] ($\sigma_{11} \to 0$)

$$\frac{p}{\rho kT} = \frac{x_1}{1 - \xi} + x_2\left(\frac{pv}{NkT}\right)_2$$

if the exact expression for $(pv/NkT)_2$ by itself is used.

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