P-V HUGONIOT FOR A MIXTURE OF GASES INTERACTING AS RIGID SPHERES

G. E. Duvall

Department of Physics
Washington State University
Pullman, Washington
99164

Internal Report

79-01

Shock Dynamics Laboratory

March 1979

ABSTRACT

The internal energy is equal to 3kT/2, as for an ideal gas, and P, V, T are related by the Abel equation

$$P(V-Nb) = NkT$$

where b is a suitable average of the molecular volumes of the two components. The pressure, P, is not the sum of the partial pressures of the two components.

Partition function for a system of N particles, including potential interactions; Maxwell-Boltzmann statistics, all particles distinguishable

$$Z = \frac{1}{h^{3N}} \int d\vec{p}_1 \int d\vec{p}_2 \cdots \int d\vec{p}_N \int d\vec{x}_1 \cdots \int d\vec{x}_N \left(\prod_{j=1}^{N} e^{-p_j^2/2m_j kT} \right) e^{-\phi/kT} \tag{1}$$

where $\phi(\vec{r}_1, \vec{r}_2, \ldots \vec{r}_N)$ is the potential energy of interaction. For N_1 particles of type 1 and N_2 of type 2, Z becomes

$$Z = \frac{1}{h^{3N} N_1! N_2!} \int d\vec{p}_1 \cdots \int dp_{N_1} \left(\prod_{j=1}^{N_1} e^{-p_j^2/2m_1 kT} \right) \int d\vec{p}_{N_1+1} \cdots \int d\vec{p}_N$$

$$\left(\prod_{j=N_1+1}^{N} e^{-p_j^2/2m_2 kT} \right) \int d\vec{x}_1 \cdots \int d\vec{x}_N \, e^{-\phi/kT} \tag{2}$$

where correction has been made for identical particles.

The integrals over $\vec{p}$ can be evaluated immediately, giving

$$Z = \frac{1}{N_1! N_2!} \left(\frac{2\pi m_1 kT}{h^2} \right)^{3N_1/2} \left(\frac{2\pi m_2 kT}{h^2} \right)^{3N_2/2} Q_N \tag{3}$$

where Q_N is the configurational partition function. (The difference between $1/N_1!N_2!$ and $1/N!$ represents the entropy of mixing.)

It has been found that for moderately dense gases the potential energy of interaction can be represented as the sum over all particle pairs of potentials which depend only on the positions of the two particles being considered:

$$\phi(\vec{r}_1, \vec{r}_2, \ldots \vec{r}_N) \simeq \sum_{i=1}^{N_1} \sum_{j=i+1}^{N_1} \varepsilon_{11}(|\vec{r}_i - \vec{r}_j|) + \sum_{i=1}^{N_1} \sum_{j=N_1+1}^{N} \varepsilon_{12}(|\vec{r}_i - \vec{r}_j|)$$

$$+ \sum_{i=N_1+1}^{N} \sum_{j=i+1}^{N} \varepsilon_{22}(|\vec{r}_i - \vec{r}_j|) \tag{4}$$

where ε_{11}, ε_{12}, ε_{22} represent the pair potential of type 1 particle interacting with type 1, type 1 with type 2, and type 2 with type 2, respectively.

It has been found that Q_N can be represented approximately by the products of interactions of single pairs*

$$Q_N \simeq Q_N^{(1)} \equiv V^N \prod_{i=1}^{N} \prod_{j=i+1}^{N} \left(\frac{1}{V^2} \int d\vec{x}_i \int d\vec{x}_j \; e^{-\varepsilon_{ij}/kT} \right) \tag{5}$$

For N_1 particles of type 1 and N_2 of type 2

$$\begin{aligned} Q_N^{(1)} = V^N & \prod_{i=1}^{N_1} \prod_{j=i+1}^{N_1} \left(\frac{1}{V^2} \int d\vec{x}_i \int d\vec{x}_j \; e^{-\varepsilon_{11}/kT} \right) \cdot \\ & \cdot \prod_{i=1}^{N_1} \prod_{j=N_1+1}^{N} \left(\frac{1}{V^2} \int d\vec{x}_i \int d\vec{x}_j \; e^{-\varepsilon_{12}/kT} \right) \cdot \\ & \cdot \prod_{i=N_1+1}^{N} \prod_{j=i+1}^{N} \left(\frac{1}{V^2} \int d\vec{x}_i \int d\vec{x}_j \; e^{-\varepsilon_{22}/kT} \right) \end{aligned} \tag{6}$$

There are $N_1(N_1-1)/2 \simeq N_1^2/2$ pairs of type 11, N_1N_2 pairs of type 12, $N_2(N_2-1)/2$ pairs of type 22, so Eq. (4) becomes

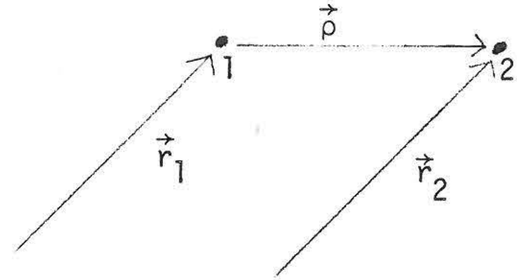
$$\begin{aligned} Q_N^{(1)} = V^N & \left(\frac{1}{V^2} \int d\vec{x}_1 \int d\vec{x}_2 \; e^{-\varepsilon_{11}/kT} \right)^{N_1^2/2} \left(\frac{1}{V^2} \int d\vec{x}_1 \int d\vec{x}_2 \; e^{-\varepsilon_{12}/kT} \right)^{N_1N_2} \cdot \\ & \cdot \left(\frac{1}{V^2} \int d\vec{x}_1 \int d\vec{x}_2 \; e^{-\varepsilon_{22}/kT} \right)^{N_2^2/2} \end{aligned} \tag{7}$$

---

* J. Kestin and J. R. Dorfman, A Course in Statistical Thermodynamics (Academic, New York, 1971), Eq. (7.13).

If the first particle is held fixed at r_1 and the second is moved through the accessible space, the integral over the second coordinate gives the interaction and the integral over the first yields the accessible volume, V. Then

$$\int\int d\vec{r}_1\, d\vec{r}_2\, e^{-\varepsilon/kT}$$



becomes

$$V\int d\vec{\rho}\; e^{-\varepsilon/kT}$$

i.e.

$$\frac{1}{V^2}\int d\vec{r}_1\int d\vec{r}_2 \quad e^{-\varepsilon/kT} \;=\; \frac{1}{V^2}\int d\vec{r}_1\int d\vec{\rho} \quad e^{-\varepsilon(\rho)/kT}$$

$$= \; V^{-1}\int d\vec{\rho} \quad e^{-\varepsilon(\rho)/kT} \;=\; 1 - V^{-1}\int d\vec{\rho}\;(1 - e^{-\varepsilon/kT}$$

where $\int d\vec{\rho} = V$. Define

$$f_{ij} \;=\; (1 - e^{-\varepsilon_{ij}/kT})$$

Then

$$(1 - V\int f_{ij}d\vec{\rho})^M \;=\; (1 - \frac{M}{MV}\int f_{ij}d\vec{\rho})^M$$

$$\equiv \; (1 - \frac{a}{M})^M \xrightarrow[M \to \infty]{} e^{-a} \qquad \text{if} \quad \frac{a}{M} \xrightarrow[M \to \infty]{} 0$$

where

$$a \;=\; \frac{M}{V}\int f_{ij}d\vec{\rho}\;.$$

Keston and Dorfman (p. 304) claim that the approximation is valid for $M = 0\;(N^e)$.

Then

$$Q_N^{(1)} \;=\; V^N\, e^{-N^2 b/V} \tag{8}$$

where

$$N^2 b \;=\; N_1^2\, b_{11} + 2N_1N_2b_{12} + N_2^2\, b_{22} \tag{9}$$

$$b_{ij} = \frac{1}{2}\int f_{ij}d\vec{\rho} = b_{ij}(T) \tag{10}$$

Then the partition function is

$$Z^{(1)} = \frac{V^N}{N_1!N_2!}\left(\frac{2\pi m_1 kT}{h^2}\right)^{3N_1/2}\left(\frac{2\pi m_2 kT}{h^2}\right)^{3N_2/2} e^{-N^2b/V} \tag{11}$$

and

$$\ln Z^{(1)} = N \ln V - \frac{N^2 b}{V} + \frac{3}{2} N \ln T \tag{12}$$

The internal energy is

$$E = kT^2 \frac{\partial \ln Z}{\partial T} = kT^2\left(-\frac{N^2}{V}\frac{db}{dT} + \frac{3N}{2T}\right) \tag{13}$$

and pressure is

$$p = kT \frac{\partial \ln Z}{\partial V} = kT\left(\frac{N}{V} + \frac{N^2 b}{V^2}\right) = nkT(1 + nb) \tag{14}$$

So b is the 2nd virial coefficient; here $n = N/V$.

For hard spheres of radius $\sigma/2$, $b = 2\pi\sigma^3/3$ and is independent of T. For the mixed gas, σ_{ij} is the closest distance of approach of the two particles. If r_1 is the hard sphere radius of type 1 and r_2 is the hard sphere radius of type 2,

$$b_{11} = \frac{16\pi}{3} r_1^3 \tag{15.1}$$

$$b_{22} = \frac{16\pi}{3} r_2^3 \tag{15.2}$$

$$b_{12} = \frac{2\pi}{3}(r_1 + r_2)^3 \tag{15.3}$$

If b is given for particles 1 and 2, r_1 and r_2 can be calculated from Eqs. (15.1) and (15.2); then b_{12} can be calculated from Eq. (15.3). For the hard sphere case

$$E = \frac{3}{2} NkT \quad \text{and} \quad p = nkT(1 + nb) \tag{16}$$

Note that

$$p = nkT(1 + nb) \simeq \frac{NkT}{V(1 - nb)} = \frac{NkT}{(V - Nb)}$$

or

$$p(V - Nb) = NkT \qquad (17)$$

which is the Abel equation.

Note that p is not the sum of the partial pressures of the two gases. For ideal mixed gases

$$p = \frac{NkT}{V} = \frac{N_1 kT}{V} + \frac{N_2 kT}{V} = p_1 + p_2 \qquad (18)$$

For the Abel gas

$$p = \frac{NkT}{V-Nb} = \frac{N_1 kT}{V-Nb} + \frac{N_2 kT}{V-Nb} \neq p_1 + p_2 \qquad (19)$$

Density of gas in a shock wave for mixture of hard sphere gases.

$$p(V - Nb) = \frac{2E}{3}$$

In the shock, $E_1 - E_o = \frac{1}{2}(p_1 + p_o)(V_o - V_1)$ or

$$p_1(V_1 - Nb) - 3p_o(V_o - Nb) = (p_1 + p_o)(V_o - V_1) \qquad (20)$$

Given p_o, p_1, V_o, b, Eq. (20) can be solved for V_1.

Then

$$p_1 \text{ is } p_o$$

$$p_2 \text{ is } p_1$$