STRUCTURE OF SIMPLE FLUIDS

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One of the most important of the many achievements of Willard Gibbs was the derivation of a single equation of universal validity, by which the properties of a macroscopic system in equilibrium could be expressed in terms of the submicroscopic mechanical properties of the molecules composing it. I wish to discuss the present status of the methods of numerical evaluation of one problem using this equation.

It is known experimentally, with a simple extrapolation from thermodynamic theory, that any system composed of real molecules at any finite nonzero temperature, T, and at infinite dilution, for which the number density, $\rho = N/V$, of molecules approaches zero, exists as a perfect gas. For the perfect gas the pressure, P, is given by the equation, $P = \rho kT$, with k equal to Boltzmann's constant, $k = 1.38 \times 10^{-16}$ ergs/deg °K. The energy of the perfect gas depends only on T, and not on the density, ρ. At sufficiently high temperature, and what is high or low depends on the type of molecule, the material remains gaseous even if the pressure is increased to any experimentally attainable value. The perfect gas equation is no longer obeyed exactly at high densities, but P remains a smooth, and presumably analytic, monotonic function of ρ. At low temperatures, below the critical temperature, condensation occurs as the density is increased. If only one species of molecule is present the condensation is abrupt on the pressure plot, that is the density increases discontinuously from that of the gas to that of the condensed phase. Below the triple point temperature the condensed phase is crystalline. (The one exception is helium for which the triple point does not exist above zero.) Above the triple point the condensed phase is a liquid.

The thermodynamic properties of a system are completely determined if one knows the equation for the energy, E_0, as a function of T in the perfect gas state, $E_0(T)$, and the equation of state, that is the equation for the pressure as a function of density and temperature, $P = P(\rho, T)$. The energy, $E_0(T)$, of the perfect gas, can be readily expressed from the Gibbs formulation as $3NkT/2$ plus a sum over the internal quantum states of the molecules, and even for relatively

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