

rates ranging from 16 ft/day down to 0.16 ft/day. It should be pointed out that there is no unanimous agreement on the lower limit of flow where diffusion may be neglected. For example, in the range between 0.1 to 0.5 ft/day, the diametrically opposed conclusion, namely, that molecular diffusion is the dominant factor, has also been reached.¹⁸ Experimental investigations in this area continue to be made.

Where molecular diffusion is negligible the present theory predicts, as may be seen by comparing Eqs. (6.8) and (6.9), that the "effective diffusion constant" $\mathfrak{D}$ is approximately proportional to the rate of flow. Experimental evidence confirms this rather well.^{18,20} In the extreme case of no

macroscopic flow, our equations break down. However, even at the very small flow rates where molecular diffusion is predominant, they still may be used to describe the observed effects if a proper value of D is selected, so as to make Eqs. (6.8) and (6.9) identical. From the phenomenological point of view, the general equation [Eq. (3.2)] offers greater flexibility than the conventional diffusion equation, through the choice of two adjustable parameters.

d. A similar theory also may be applied to other displacement processes such as the replacing of one kind of ion by another in ion-exchange columns. This was done by Thomas,¹⁹ in dealing with the kinetics of ion exchange and chromatography, and by Polya²⁰ to treat the analogous problem of gravel transport by rivers.

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¹⁸ R. J. Blackwell, J. R. Rayne, and W. M. Terry, *J. Petrol. Technol.*, XI, 1 (January, 1959).

¹⁹ H. C. Thomas, *J. Am. Chem. Soc.* 66, 1664 (1944), and *Ann. N. Y. Acad. Sci.* 49, 161 (1948).

²⁰ G. Polya, *Zur Kinematik der Geschiebebewegung* (Mitteilung der Versuchsanstalt für Wasserbau an der Eidg. Techn. Hochschule, Zürich, Switzerland, 1937).

Shock Hugoniot for Liquid Argon

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Shock Hugoniot for liquid argon are calculated using equations-of-state obtained from the Monte Carlo method and the Lennard-Jones-Devonshire cell theory, using an experimentally determined pair potential. Agreement with presently available experimental data is poor.

1. INTRODUCTION

MANY statistical mechanical theories of the equation of state of dense molecular systems make use of the assumption of additivity of intermolecular forces, which states that the total interaction energy can be expressed as a sum of terms referring to the interactions of isolated pairs of molecules. It is known that this assumption is not exactly correct, and the degree of its validity has been the subject of considerable investigation.¹ However, there is very little, if any, experimental information pertaining to the repulsive region of the pair potential of intermolecular force.

The additivity assumption can of course be tested by comparing with experiment the results of statistical calculations based on experimentally determined pair potentials. From the theoretical standpoint, this approach has been hindered by the lack of accurate data on the repulsive portion of the pair potential, and of an accurate and tractable statistical theory. These difficulties have been partly overcome in recent years. The molecular scattering method for the determination of pair potentials has been extended out to distances near the crossover,² and the Monte Carlo method of calculation³ is free of the major uncertainties in

¹ L. Jansen, *Some Aspects of Molecular Interactions in Dense Media* (Martinus Nijhoff, The Hague, Netherlands, 1955).

² I. Amdur and E. A. Mason, *J. Chem. Phys.* 22, 670 (1954); *Phys. Fluids* 1, 370 (1958).

³ W. W. Wood and F. R. Parker, *J. Chem. Phys.* 27, 720 (1957) (further results are to be published).