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HIGH-PRESSURE AND HIGH-TEMPERATURE BEHAVIOR OF SIMPLE AND COMPLEX MOLECULAR LIQUIDS*

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ABSTRACT

Recent theories in statistical mechanics and intermolecular forces are used to explain the shock-wave data of inert gases, diatomic molecules, and hydrocarbons.

INTRODUCTION

The conditions over which thermodynamic data can be obtained by shock-wave techniques range to as high as hundreds of gigapascals (1 GPa = 10 kbar) and temperatures of several electron volts (1 eV = 11604.5 K). The high-temperature and high-pressure nature of the shock-wave data can provide us with fundamental information regarding intermolecular repulsions, vibrational excitations, many-body forces, density-dependence of electronic energy levels, and anisotropic forces in polyatomic molecules. In this paper recent theoretical methods in statistical mechanics and intermolecular forces are combined to extract such information from the shock-wave data of monatomic (Ar and Xe) and polyatomic (H_2 , N_2 , and hydrocarbons) systems.

In a shock-wave experiment, one measures the shock velocity U_s and the particle velocity U_p . The pressure, P , the volume, V , and the energy, E , are determined by the Rankine-Hugoniot relations. A theoretical shock-wave curve (Hugoniot) is computed by using an equation of state and finding the locus of P , V , E points which satisfies:

$$E = E_0 + \frac{1}{2} (P_0 + P) (V_0 - V) \quad (1)$$

INERT GASES: ARGON AND XENON

Argon. Recently, accurate shock-wave data¹ of liquid Ar have been obtained in the P -range 40-91 GPa, and up to three times the liquid density at 1 atm and at calculated temperatures to 26000 K. In this range of T only two processes may take place: the intermolecular repulsions and, at $T > 14000$ K, the electronic excitations. At $T < 14000$ K, only the intermolecular repulsion is important. Here P and E are computed² from the Helmholtz energy A :

$$A = A^0(d) + \frac{1}{2} \rho \int g^0(r, d) \phi(r) dr, \quad (2)$$

where ρ = density. The free energy A^0 and the radial distribution function g^0 of the reference system (taken to be the system with r^{-12} repulsion) by the corresponding quantities for hard spheres having diameter d with a correction term to take account for the soft repulsion. The diameter d is determined in turn by minimizing Eq. (2). The shock-wave data can be satisfactorily represented if the pair potential $\phi(r)$ of Ar is chosen to be^{1a}

$$\phi(r) = \epsilon \left\{ \frac{6}{\alpha-6} \exp [\alpha(1-r/r^*)] - \frac{\alpha}{\alpha-6} (r^*/r)^6 \right\} \quad (3)$$

with $\alpha = 13$, $\epsilon/k = 122$ K, and $r^* = 3.85$ A.

Figure 1(a) shows theoretical Hugoniot data of Ar using different $\phi(r)$'s and the experimental data (barga^{1a} and dots^{1b}). The computed Hugoniots using the Parson-Siska-Lee (PSL)^{3a} (inferred from the beam-scattering data) and SW [Eq. (3)] potentials are in excellent agreement with the shock-wave data. The Hugoniot computed from the Barker-Fisher-Watts (BFW)^{3b} potential is too soft and the HFDC result^{3c} is too stiff. The estimated Hugoniot temperatures in $V = 14.5$ to 13.25 cm³/mol are from 6300 to 13000 K. This implies that the Hugoniot experiments can probe the repulsive interaction down to about 2.2 A. In comparison, the beam data is valid over the range from 1.70 to 2.65 A. The PSL potential solely measures the Ar-Ar pair interaction, whereas the SW potential contains many-body effects. Thus, a close agreement between the two results implies that the many-body forces in Ar are small.

Fig. 1 Experimental and theoretical Hugoniots of liquid Ar: (a) low-P portion and (b) high-P portion. See the text for explanation of the notations.

At $T > 14000$ K, an appreciable number of electrons are thermally excited. A model that treats the excited electrons by semiconductor theory has been developed recently;^{1a}

$$E = E_{ins} + \sum_i \Delta E_i N_i + E_t, \quad (4)$$

$$P = P_{\text{ins}} - \sum_i \frac{\partial \Delta E_i}{\partial V} N_i + P_t, \quad (5)$$

where the subscripts ins denote the insulator properties computed from Eqs. (2) and (3), and the subscripts t represent electronic contributions. ΔE_i is the volume-dependent energy gap between the 3p state and the 4s (or 3d) band and N_i is the number of electrons excited. The energy gap was calculated from the Wigner-Seitz (WS) and Augmented Plane Wave (APW) methods.

Figure 1(b) shows the experimental and theoretical Hugoniot of Ar. The two lower curves (A) and (B) are calculations incorporating the volume-dependent WS and APW band gaps, respectively. Both curves agree satisfactorily with experiment. For comparison, calculations (D) without electronic excitation and calculations (C) including only the constant band gap (14.2 eV) begin to deviate from the lower curves at 40 GPa. At the highest P, theory predicts that 0.12 electrons/atom have been excited. By absorbing some of the shock energy the excited electrons act as thermal sinks keeping the temperature down and thus lowering the pressure. In addition, the decreasing 3p-3d band gap contributes a negative term to the P. These electronic thermal processes lead to the observed softening of the experimental Hugoniot.

Xenon. Shock experiments of liquid Xe also fit this picture.⁴ The Hugoniot data is consistent with an insulator model to 25 GPa. However, near 50 GPa at 2.5-fold compression the APW calculations predict the band gap to decrease from 9.3 eV at 1 atm to about 6 eV. Therefore, as in the case of Ar, the combination of high temperatures and narrowing band gap causes an observed softening of the Hugoniot curve. We also found that $\phi(r)$ used in calculating the Xe Hugoniot and that obtained from high-energy molecular beam studies agree remarkably well. These potentials give 0 K-solid isotherms in good agreement with the recent measurements of Syssen and Holzapfel⁵ up to 10 GPa.

DIATOMIC SYSTEMS: MOLECULAR HYDROGEN AND NITROGEN

H₂. Van Thiel et al.⁶ have performed shock-wave experiments in which the normal liquid D₂ was compressed by a factor of seven. Ross⁷ found an effective potential that fits the experimental data. To estimate the many-body contributions in the effective potential, we have carried out two- and three-body potentials.⁸ Figure 2 shows the ab initio $\phi(r)$ together with other $\phi(r)$'s. These $\phi(r)$'s differ widely because most of them are extrapolated beyond the ranges of validity. In Fig. 2, the solid lines indicate those parts of $\phi(r)$ which are reliable.

There are two classes of $\phi(r)$'s; those based on the condensed-state data (shock-wave⁷ and static compression^{9a}) and those based on measurements that include only the two-body potential [molecular-beam (MB),^{9b} the second virial coefficient (B₂),^{9c} and the transport coefficients (transp)^{9d}]. Figure 2 shows that the former class of potentials lies well below the ab initio $\phi(r)$. This is most likely due to the many-body effect in the condensed-state data. Among $\phi(r)$'s belonging to the second class, transp $\phi(r)$ is valid to 4.2 bohr, hence the most appropriate. Both the ab initio and transp $\phi(r)$ show a reasonable agreement within $4.3 < r < 4.8$ bohr. At $r \approx 5$ bohr, the two agree less well. There is a similar disagreement between the ab initio $\phi(r)$ and both the B₂ and the MB $\phi(r)$'s. This may be due to the electron correlation energy that is not accounted for by our ab initio calculations. The MB $\phi(r)$ and the B₂ $\phi(r)$ are based on the data to 300-400 K. These temperature ranges lie outside the range of the ab initio $\phi(r)$. Since these data represent integrated effects over r, it may be possible to find a self-consistent $\phi(r)$ that agrees with the ab initio $\phi(r)$ at $r \lesssim 5$ bohr and at the same time can explain the experimental data.

Fig. 2 H_2-H_2 potentials computed from theoretical and experimental methods as discussed in the text. The dashed lines indicate the extrapolation beyond the ranges of validity.

The calculation also showed that the anisotropy in $\phi(r)$ is relatively small. For example, at $r = 3$ bohr, the highest rotational barrier is ≈ 4000 K. Therefore, in a shock-wave environment where T is high (≈ 7000 K), the use of an isotropic potential is justified.

N_2 . There are experimental Hugoniot data¹⁰ of N_2 to 63 GPa which corresponds to 3.3-fold compression of the normal liquid N_2 . Since the anisotropic interaction of nitrogen may be important in interpreting the shock-wave data, we have computed^{11a} the N_2-N_2 $\phi(r)$ by the *ab initio* SCF method and the approximate Gordon-Kim-Rae (GKR) model that uses less computing time.

Figure 3(a) shows the calculations on five different orientations. The most striking feature is a large anisotropic interaction of N_2 . At $r = 5.5$ bohr which lies close to the highest compression of the experiment, the anisotropy in $\phi(r)$ accounts for nearly 3 eV—too large to neglect compared to the shock temperature. We also note that both the SCF and the GKR potentials are in reasonable agreement (except for L-geometry) if $\phi(r) \gtrsim 10^{-2}$ hartree. Figure 4(a) shows a loop in $\phi(r)$ at $r \approx 4.8$ bohr in the L-geometry. This loop is due to a crossing of the highest occupied orbital, of the supermolecule N_2-N_2 , by the lowest unoccupied level to which electrons are transferred. The observed energy level crossing may have a bearing on the metal-insulator transition for nitrogen. At large r , the quadrupole interaction starts to dominate. Since the quadrupole moment depends sensitively on the basis set, the *ab initio* results differ from the corresponding GKR results.

To use the N_2-N_2 $\phi(r)$ in the Hugoniot calculation we fit $\ln \phi(r)$ by an analytic form. The Hugoniot^{11b} is computed from the free energy A :

$$\begin{aligned} A/(NKT) = & 3.5 \ln T + \ln(1 - e^{-\theta/T}) \\ & + \mu/(NKT) - \sum_i \ln [1 + \exp(\frac{\mu - \Delta E_i}{KT})] + A_{\text{conf}}/(NKT), \end{aligned} \quad (6)$$

where θ is 0.292 eV and μ is the chemical potential. The energy gap ΔE_i 's are determined from the excited-state levels of two N_2 . The configurational free energy A_{conf} was computed by the Lennard-Jones-Devonshire cell model, in which the equilibrium orientations of N_2 molecules are chosen to minimize the static energy.

Figure 3(a) shows a reasonable agreement between the theoretical Hugoniots obtained from the above model and experimental points at $P < 30$ GPa. At $P >$

Fig. 3 (a) SCF potentials of two N_2 based on the ab initio and the GKR methods as discussed in the text; (b) theoretical and experimental¹⁰ Hugoniot of N_2 .

30 GPa, however, the theoretical points lie above the experimental points. As is shown in Fig. 3(b), contribution by the electronic excitation is unimportant. Since the Hugoniot of Ar is insensitive to many-body contributions, we expect a similar behavior for N_2 . If this is so, the deviation between the theoretical and experimental Hugoniot may be due to the cell-model assumption that constrains the neighboring molecules to be fixed in space. Another explanation is the possibility of formation of a monatomic or metallic phase.

HYDROCARBONS

Our analysis of the hydrocarbon Hugoniot uses the available Hugoniot data.¹² We classify the Hugoniot data into groups with different ratios of hydrogen to carbon atoms (H:C) contained in the hydrocarbons. Figure 4 shows Hugoniot of eight different hydrocarbons with four different H:C ratios.

We wish to know if the Hugoniot data show a systematic behavior. A systematic behavior become apparent if all the P vs V Hugoniot are displayed in one figure. Such a plot shows that Hugoniot with the same H:C ratio group together at high pressure and form a single curve and those with different H:C ratios form separate high-P groups. It also shows that at any given P (~ 10 GPa) the specific volumes are ordered in such a manner that the group with a larger H:C ratio has a larger volume. The observed regularity indicates that the high P and high T realized during the shock compression might have broken the H-C bonds to form two different covalent bonds—H-H bonds to form H_2 and C-C bonds to form a diamondlike structure.

Fig. 4 Experimental (points) and theoretical (lines) Hugoniots of hydrocarbons. The theoretical Hugoniots are only applicable at high- U_s portions.

Our analysis is based on the Mie-Grüneisen equation:

$$P(V,T) = P(V, 0 K) + (\gamma/V) [E(V,T) - E(V, 0 K)] , \quad (7)$$

where γ is the Grüneisen parameter. We assume that $V(P, 0 K)$ and (V/γ) at a given P are the sums of the corresponding quantities for pure hydrogen and carbon, weighted by the relative amounts of C and H atoms in the hydrocarbons. This procedure requires the knowledge of $V(P, 0 K)$ and (V/γ) (assumed to be constant) for both C and H. In the case of C, in the T- and P-range (~ 1000 K, ~ 10 GPa) of interest, the expected phase is diamond whose 0 K-isotherm and γ/V at 1 atm are obtained from available experimental data. We use theoretically based data on condensed H_2 .

In Fig. 4 the theoretical U_s vs U_p Hugoniots are seen to agree, within the pressure range of interest, with the corresponding experimental data remarkably well. From this one can draw a conclusion that the hydrocarbon data can be satisfactorily described by the carbon data in the diamond phase and the hydrogen data in a condensed molecular phase.

In summary, we have presented theoretical models for molecules in condensed phases. The analyses have required considerations of electronic excitations, many-body forces, anisotropic interactions, and molecular dissociations. We also hope to have demonstrated that there is a potentially fruitful area for close coordination of experimental and theoretical studies to develop even more reliable theories of condensed matter.

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