

Three-Body-Potential Contribution to the Structure of Krypton Gas

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A series of careful diffraction experiments on krypton gas have been done over a range of densities along the room-temperature isotherm. These data are compared with Monte Carlo calculations based on the (known) pair potential for krypton. Small differences are observed which are interpreted in terms of the three-body potential. It is probable that some experimental information concerning the short-range part of this potential can be derived from these data.

It has been known for many years that the coefficients of the virial expansion for the pressure of the noble gases must be discussed in terms of both pair and higher-order forces. For example, this virial series can be written as

$$P/kT = \lim_{\rho \rightarrow 0} [\rho + \rho^2 B(q, T) + \rho^3 \{C_1(q, T) + C_2(q, T)\} + O(\rho^4)], \quad (1)$$

where P is the pressure, k is the Boltzmann's constant, T is the temperature, and ρ is the density. In this formula

$$B(q, T) = -\frac{1}{2} \int f(r) e^{i\vec{q} \cdot \vec{r}} d^3r,$$

$$C_1(q, T) = -\frac{1}{3} \iint f(r) f(s) f(r-s) e^{i\vec{q} \cdot \vec{r}} d^3r d^3s,$$

$$C_2(q, T) = -\frac{1}{3} \iint [f(r) + 1][f(s) + 1][f(|\vec{r} - \vec{s}|) + 1][\exp(-\beta u_3(\vec{r}, \vec{s})) - 1] e^{i\vec{q} \cdot \vec{r}} d^3r d^3s,$$

where \vec{r} is the displacement between a given pair of atoms, \vec{s} is the displacement between one of these atoms and a third atom, $f(r) = e^{-\beta u_2(r)} - 1$, $\beta = 1/kT$, u_2 and u_3 are the pair and triplet potentials, respectively, and \vec{q} is the wave vector.

While a great deal of information has been extracted for many years from Eq. (1), it has not been possible to examine the q dependence of the coefficients. Since $f(r)$ may be calculated from $u_2(r)$, the coefficients $B(q, T)$ and $C_1(q, T)$ may be calculated once the pair potential is given.¹ However, $C_2(q, T)$ depends upon the three-body potential of which only the long-range triple-dipole term² is known. Thus it would be advantageous if the q dependence of the function C_2 could be obtained. This can be done in principle by performing a series of diffraction measurements with gases, as may be seen by considering the virial series for the pair correlation function. We get the following expression for the direct correlation function

$$c(q) = -2B(q, T) - 3\rho[C_1(q, T) + C_2(q, T)] + O(\rho^2), \quad (2)$$

where $c(q)$ is the direct correlation function equal to $[1 - S^{-1}(q)]/\rho$ and $S(q)$ is the structure factor given by

$$S(q) = 1 + \rho \int [g(r) - 1] e^{i\vec{q} \cdot \vec{r}} d^3r, \quad (3)$$

and the pair correlation function $g(r)$ may be expanded as

$$g(r) = f(r) + 1 + \rho [f(r) + 1] \left\{ \int f(s) f(|\vec{r} - \vec{s}|) d^3s + \int [f(s) + 1][f(|\vec{r} - \vec{s}|) + 1][\exp(-\beta u_3(\vec{r}, \vec{s})) - 1] d^3s \right\} + O(\rho^2). \quad (4)$$

In order to employ Eq. (2) usefully, a number of accurate measurements of $S(q)$ are required over a range of densities in the gas phase. We have measured the structure factor for krypton gas at room temperature (297 K) and at twelve densities from $\rho = 0.25 \times 10^{27}$ atoms/m³ (~ 10 atmospheres pressure) to $\rho = 5.15 \times 10^{27}$ atoms/m³ (~ 10 atmospheres pressure) in the range 0.2

$\leq q \leq 4.0 \text{ \AA}^{-1}$ using the neutron diffraction technique. For nine densities the precision was $\sim \pm \frac{1}{2}\%$ for $q > 0.4 \text{ \AA}^{-1}$ and of the order of $\pm 1\%$ for $q < 0.4 \text{ \AA}^{-1}$, and for three densities (i.e., 1.52, 1.96, and 2.43×10^{27} atoms/m³) this division occurs at 1 \AA^{-1} . An example of the data (for $\rho = 2.88 \times 10^{27}$ atoms/m³) is given in Fig. 1, compared

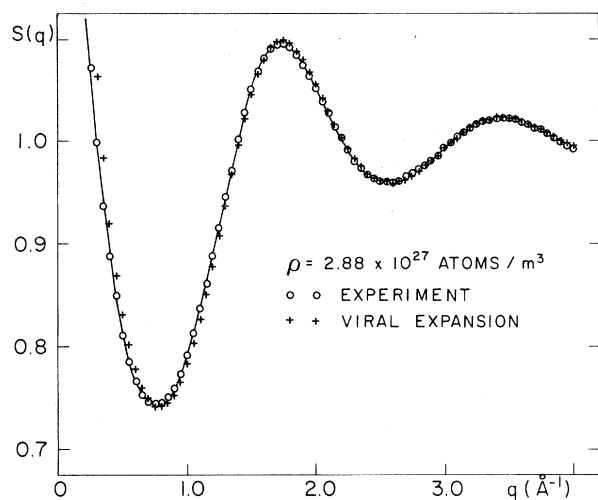


FIG. 1. The structure factor for krypton gas at 297 K and 2.88×10^{27} atoms/m³. The circles and full line show the experimental values, while crosses (each cross is calculated for a q corresponding to each circle) show the results predicted by a pair theory based upon the pair potential of Barker *et al.* (Ref. 1).

with a prediction based on the virial series (Eq. 2) using the pair potential of Barker *et al.*¹ alone [i.e., $C_2(q, T) = 0$].

The general agreement is very satisfactory but there are differences greater than the errors which we believe are due to three-body forces.

All our data were Fourier transformed by extending the range of q from 4 \AA^{-1} to 20 \AA^{-1} with use of theoretical curves based on the potential of Barker *et al.*¹ It is readily shown that in this range and at these densities only the term involving $B(q, T)$ is significant (in contrast to the lower range of q , where higher terms are important). In Fig. 2 we have plotted the height of the principal peak in $g(r)$ as a function of density. For the 297-K isotherm the peak height decreases with increasing density until $\rho \sim 6 \times 10^{27}$ atoms/m³. These results are compared to the results of Monte Carlo calculations² of $g(r)$ using only two-body forces. It is known that the long-range triple-dipole force³ suppresses the peak of $g(r)$, and this suppression of the experimental peak height below the theoretical two-body data is readily apparent.

Finally, we have plotted our data at each momentum transfer q as a function of density. Some examples are shown in Fig. 3, where the quantity plotted is the direct correlation function $c(q)$. The slope of these curves is the coefficient of ρ in Eq. (2), and the full lines show the quantity

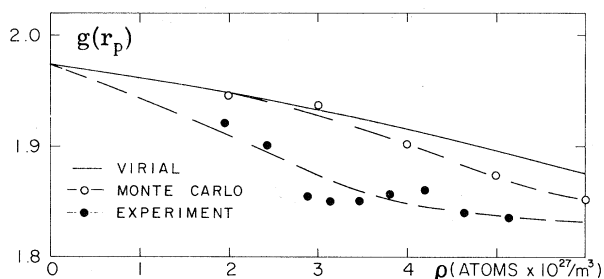


FIG. 2. Principal peak height of $g(r)$ for krypton gas at 297 K. The full line is a virial calculation and the open circles are Monte Carlo results based on the pair potential alone. The solid circles are the experimental results. The dashed lines have been drawn "by eye" through the open and closed circles. r_p is the peak position.

$[-2B_2(q, T) - 3\rho C_1(q, T)]$, so that the difference between the line and the points is due to $C_2(q, T)$. It is clear that we are able to measure the term $C_2(q, T)$ over a range of q values. At $q = 0$, we have plotted the well known PVT result.⁴ As q increases, the effect of $C_2(q, T)$ initially increases and then decreases, so that at $q = 0.5 \text{ \AA}^{-1}$ it

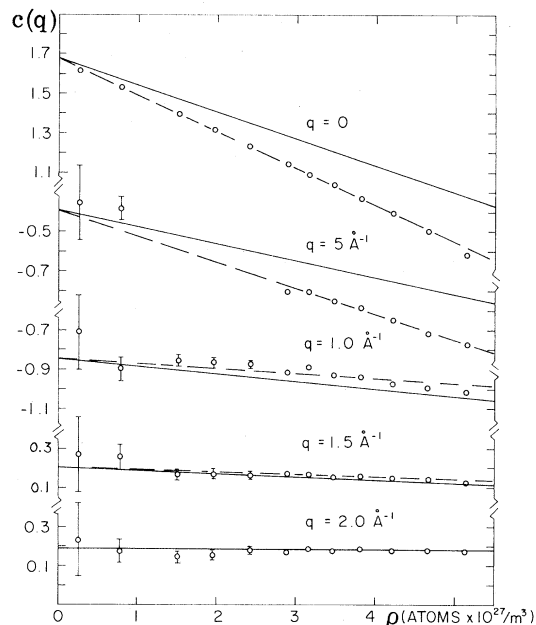


FIG. 3. The direct correlation function plotted as a function of density for several values of q ($q = 0$ corresponds to PVT data). The full line is calculated from the pair potential and Eq. (2) while experimental values are shown as open circles. The dashed line is the best-fitting straight line through the data.

is approximately equal to that at $q=0$. From approximately $q=1.0 \text{ \AA}^{-1}$ to $q=1.5 \text{ \AA}^{-1}$ it has the opposite sign to that at $q=0$ and by 2 \AA^{-1} it is no longer measurable. A preliminary analysis of the variation with q suggests that the data are sensitive to the short-range three-body terms as well as the triple-dipole term.

A fuller account of this project will be published elsewhere.

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Calculation of s - p Coherence in Hydrogen after Electron Capture

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The electron capture by protons in a gas target is calculated in the Oppenheimer-Brinkman-Kramers approximation. The complete density matrix for the $n=2$ hydrogen level is established. Electric-field-induced s - p coherence quantum beats are investigated. Good agreement with the experimental data is achieved.

Recently, Sellin *et al.*¹ found "a high degree of excitation coherence in electron capture to mixed-parity $n=2$ states by fast protons in gases." This result was essentially derived from the intensities I^+ (I^-) of Ly α -Stark quantum beats in an external electric field F^+ (F^-) parallel (antiparallel) to the beam axis, exploiting the fact that the difference signal ($I^+ - I^-$) is directly proportional to the coherence density-matrix element and odd in the electric field² while the sum signal ($I^+ + I^-$) depends only on the incoherent part of the excitation (terms with even powers in the field).

In this Letter we briefly report on a theoretical interpretation of the new data given in Ref. 1. It is based on the, to our knowledge, first calculation of the complete ($n=2$) density matrix including the coherence part. For the sake of simplicity we restrict ourselves to an extended Oppenheimer-Brinkman-Kramers (OBK) approximation.

In the following treatment we divide the complete interaction process into three steps: (a) the electron capture at small projectile-target distances ($\leq R_0$), (b) the post-collision interaction at large distances ($> R_0$), and (c) the final evolution of the density matrix under the influence of the applied electric field.

(a) Because of the short interaction time in the energetic ion-atom collision ($\tau_c \approx 10^{-16}$ s), the capture process is essentially spin independent

and is not influenced by external fields. Charge transfer from the helium ground state (binding energy ϵ_i) to $n=2$ hydrogenic orbital angular momentum states (binding energy ϵ_j) can therefore be calculated by ignoring the fine and hyperfine structures of the projectile. The impact-parameter-dependent capture amplitude at projectile velocity v in OBK approximation is given by³

$$A_{lm}(\vec{b}) = -i \int_{-\infty}^{R_0/v} dt \langle \varphi_{lm} | -|\vec{\mathbf{F}}_p|^{-1} | \varphi_{\text{He}(1s)} \rangle. \quad (1)$$

Atomic units are used and the beam direction is chosen as quantization axis. The distance between the active electron and the projectile is denoted by $|\vec{\mathbf{F}}_p|$. The wave functions used in Eq. (1) must include the translation factors that account for the projectile-target relative motion. Because of the exponential decay of the overlap integral at large distances, the upper bound in Eq. (1) can be pushed to $R_0/v = \infty$. Since in the OBK approximation the s - p coherence phase turns out to be rather insensitive to the details of the atomic-target orbital, we approximate the He ground state by a hydrogenlike wave function scaled to charge Z_i .

After the charge transfer, the unnormalized excited-state ($n=2$) density matrix

$$\sigma_{lm, l'm'} = \int d^2b A_{lm}(\vec{b}) A_{l'm'}^*(\vec{b}) \quad (2)$$

contains only five nonvanishing elements. (This