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LETTER TO THE EDITOR

Direct determination of the helium interatomic core potential by neutron scattering

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Abstract. The three derivatives of the static structure factor $S(k)$ with respect to density n , temperature T and wavenumber k are determined for He at $n = 18.7 \text{ nm}^{-3}$ and $T = 13.3 \text{ K}$ by means of neutron scattering. Using an exact scaling relation valid for interatomic core potentials $\varphi(r) = \varepsilon(\sigma/r)^l$, the results for helium are consistent with a power $l = 18 \pm 2$.

The determination of the effective two-particle interatomic potential $\varphi(r)$ of noble gas fluids by means of neutron scattering experiments has been a long standing problem in equilibrium statistical physics [1]. In principle, the full interatomic potential $\varphi(r)$ can be deduced directly from the measured static structure factors $S(k)$ at low number densities n using the fact that the pair correlation function $g(r)$ (which is the spatial Fourier transform of $S(k)$) is, for $n \rightarrow 0$, given by $g(r) = \exp(-\varphi(r)/k_B T)$, where T is the temperature of the fluid and k_B is the Boltzmann constant. So far, a reliable direct determination of $\varphi(r)$ from low density data for $S(k)$ has only been achieved for argon [2] due to its exceptionally large neutron scattering cross section. At finite densities, Meyer *et al* [3, 4] have shown that information about the interatomic (repulsive) core forces can be deduced from $S(k)$ at large wavenumbers k (i.e. $k > 2 \text{ \AA}^{-1}$). They applied a formalism based on softened hard sphere interactions [5, 6], i.e. for interactions given by

$$\varphi(r) = \varepsilon(\sigma/r)^l \quad (1)$$

with ε the interaction energy, σ the effective diameter, r the distance between two particles and l the power of the interaction law. Meyer *et al* find [3, 4] for high densities that $l = 15$ for Ne and that $l = 19$ for Ar (in agreement with the argon results for $\varphi(r)$ of [2]). Here we apply a new method to determine the power l for helium. In fact we determine by neutron scattering the derivatives of $S(k)$ with respect to n , T and k , and use an exact relation between these three derivatives and l which holds for the potentials $\varphi(r)$ of equation (1) and which is valid for all n and T and for *all* k . Thus we obtain $l = 18 \pm 2$ for helium in the region $4 \text{ K} < T < 22 \text{ K}$ and $18 \text{ nm}^{-3} < n < 25 \text{ nm}^{-3}$.

The experiment was performed using the time-of-flight diffractometer LAD at the Rutherford Appleton Laboratory. The cross section of the incident neutron beam was $1.5 \times 4.0 \text{ cm}^2$. The sample container consisted of a vanadium cylinder with height 5 cm,

Table 1. Thermodynamic (n, p, T) states of helium [10] for which $S(k)$ is measured.

n (nm ⁻³) \ T (K)	4.3	13.3	21.9
18.7	1.12 bar	40.3 bar	78.4 bar
22.0	—	58.3 bar	—
24.8	—	81.6 bar	—

diameter 2 cm and wall thickness 0.05 cm (maximum pressure 90 bar). To avoid large inelasticity corrections we only used the small angle detector groups (at 5, 10, 20 and 35°). We calculated the static structure factors $S(k)$ from the time-of-flight spectra using the LAD standard correction programs [7, 8]. We obtained the helium $S(k)$ data for five thermodynamic states (see table 1): $n = 18.7 \text{ nm}^{-3}$, $T = 4.3 \text{ K}$, 13.3 K and 21.9 K , and $T = 13.3 \text{ K}$, $n = 22.0 \text{ nm}^{-3}$ and 24.8 nm^{-3} . A full account of the experimental results will be given elsewhere [9]. $S(k)$ at $T = 13.3 \text{ K}$ and $n = 18.7 \text{ nm}^{-3}$ and its derivative $\partial S(k)/\partial k$ are shown in figure 1. From the five $S(k)$, we obtained the derivatives of $S(k)$ with respect to n and T by numerical differentiation.

To interpret the results, we note that for the interatomic potentials $\varphi(r)$ of (1), $S(k)$ is given by

$$S(k) = S_l(k\sigma(T), n\sigma(T)^3) \quad (2)$$

where

$$\sigma(T) = \sigma(\varepsilon/k_B T)^{1/l} \quad (3)$$

$$S_l(x, y) = \frac{1}{N} \sum_{p, q=1}^N \left[\int' ds_1 \dots \int' ds_N \exp[-\Phi_l + i \mathbf{x} \cdot (s_p - s_q)] \right. \\ \left. \times \left(\int' ds_1 \dots \int' ds_N \exp(-\Phi_l) \right)^{-1} \right]. \quad (4)$$

Here \mathbf{x} is a reduced wave vector with length $x = |\mathbf{x}|$, $x = k\sigma(T)$ is the reduced wave-number and $y = n\sigma(T)^3$ is the reduced number density. Furthermore

$$\Phi_l = \frac{1}{2} \sum_{\substack{i, j=1 \\ i \neq j}}^N |s_i - s_j|^{-l} \quad (5)$$

is the reduced total interaction potential, and the integration in equation (4) over the reduced location s_j of particle j runs over

$$\int' ds_j \dots = \int_0^{(N/y)^{1/3}} ds_{jx} \int_0^{(N/y)^{1/3}} ds_{jy} \int_0^{(N/y)^{1/3}} ds_{jz} \dots \quad (6)$$

Therefore, in the thermodynamic limit (x, y constant; $N \rightarrow \infty$), $S_l(x, y)$ is a function of l , x and y only. As a consequence of this result and of equations (2) and (3) one finds straightforwardly that the power l of the interaction potential is given by

$$l = (k\partial S(k)/\partial k + 3n\partial S(k)/\partial n)/(-T\partial S(k)/\partial T) \quad (7)$$

valid for all k , n and T . Here the partial derivative with respect to k is taken at constant

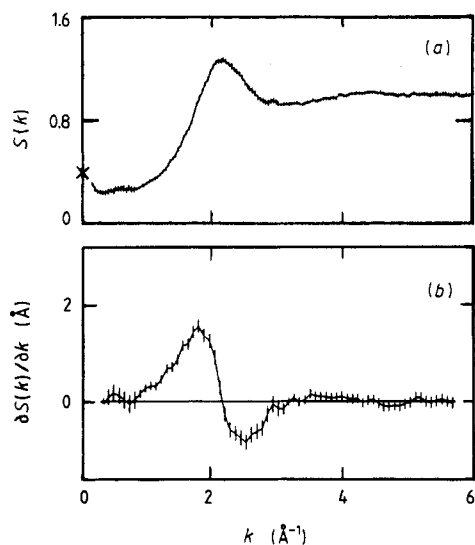


Figure 1. (a) $S(k)$ of helium at $n = 18.7 \text{ nm}^{-3}$ and $T = 13.3 \text{ K}$ as a function of k . $S(0)$ (cross at $k = 0$) is taken from compressibility data [10]. (b) Partial derivative $\partial S(k)/\partial k$ calculated directly from (a).

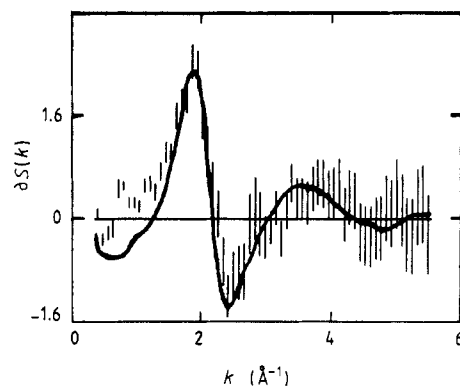


Figure 2. Partial derivatives of $S(k)$ for helium at $n = 18.7 \text{ nm}^{-3}$ and $T = 13.3 \text{ K}$ as functions of k . Error bars: $k\partial S(k)/\partial k + 3n\partial S(k)/\partial n$. Full curve: $-18T\partial S(k)/\partial T$.

n , T ; to n at constant k , T , and to T at constant k , n . Equation (7) includes the hard sphere potential for which $\partial S(k)/\partial T = 0$ and $l = \infty$.

In figure 2 we show $k\partial S(k)/\partial k + 3n\partial S(k)/\partial n$ (at $n = 18.7 \text{ nm}^{-3}$, $T = 13.3 \text{ K}$) as a function of k . For a large k -region ($1 \text{ \AA}^{-1} < k < 6 \text{ \AA}^{-1}$) we find this quantity to be proportional to $T\partial S(k)/\partial T$ (cf. (7)). This is shown in figure 2 where $-T\partial S(k)/\partial T$ is displayed multiplied with $l = 18$. In fact, we find from the present results for helium (at $n = 18.7 \text{ nm}^{-3}$, $T = 13.3 \text{ K}$) that $l = 18 \pm 2$. Our results show furthermore that $T\partial S(k)/\partial T$ at $n = 18.7 \text{ nm}^{-3}$ is virtually constant when T varies from $T = 4.3 \text{ K}$ to $T = 29.3 \text{ K}$. Also, the shape of $k\partial S(k)/\partial k + 3n\partial S(k)/\partial n$ at $T = 13.3 \text{ K}$ does not change significantly from $n = 18.7 \text{ nm}^{-3}$ to $n = 24.8 \text{ nm}^{-3}$ —at least for $k > 1 \text{ \AA}^{-1}$. We conclude therefore that the result $l = 18 \pm 2$ is relevant for helium in the whole region $18 \text{ nm}^{-3} < n < 25 \text{ nm}^{-3}$ and $4 \text{ K} < T < 22 \text{ K}$.

We end with a number of remarks.

We find that the helium value $l = 18 \pm 2$ is not significantly different from the neon and argon values for l . Thus, it appears that the law of corresponding states holds for $\varphi(r)$ of the noble gas fluids He, Ne, Ar.

A direct comparison between the $\varphi(r) = \varepsilon(\sigma/r)^l$ potential and the Lennard-Jones potential $\varphi_{LJ}(r) = 4\varepsilon[(\sigma/r)^{12} - (\sigma/r)^6]$ leads to an estimation of l . For instance, if the two potentials are made to coincide at 4ε , then this would render a value of $l \approx 17$.

It might be interesting to see whether l depends on the density. If so, this would mean that $\varphi(r)$ is an effective pair potential, effectively taking into account the (density dependent) three- (and four-) body forces.

We expect that equation (7) breaks down for n , T near the critical point, in particular for small k —since the attractive part of the interatomic potential will be seen most clearly

in that region (i.e. $k < 1 \text{ \AA}^{-1}$). It is unclear at present if (7) will hold then for microscopic values of k , i.e. for $k \approx 2 \text{ \AA}^{-1}$ near the first maximum of $S(k)$.

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