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LETTER TO THE EDITOR

The structure of liquid neon: an anomaly resolved

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Abstract. It is shown that the structure $g(r)$ of liquid neon can be regarded as resulting from an effective interatomic pair-potential of Lennard-Jones 12–6 form with parameters from thermodynamics, provided due account is taken of quantum corrections. Liquid neon therefore 'corresponds' with liquid argon and is not anomalous, as appeared previously to be the case. The novel and useful observation is made that the quantum corrections to $g(r)$ tend to be small for large r.

It is well known that the assumption of a pairwise Lennard-Jones 12–6 (LJ) potential

$$\varphi(r) = 4\varepsilon[(\sigma/r)^{12} - (\sigma/r)^6]$$

with values of the energy parameter ε and the distance parameter σ given by the gas-phase properties: i.e. $\varepsilon/kK = 119.8$ and $\sigma = 3.405$ Å (Michels *et al* 1949) yields thermodynamic properties of liquid argon which are in remarkable agreement with experiment (McDonald and Singer 1967, 1969, Barker and Henderson 1976). Moreover, and this is not unconnected, the structure of liquid argon is also given correctly; the virtually exact simulation results of Verlet (1968) agree remarkably well with experiment, e.g. see figure 6 of Yarnell *et al* (1973).

This is not to deny that the true argon pair-potential differs significantly from the LJ form (Barker *et al* 1971). In condensed phases the effect of the three-body potential (Axilrod and Teller 1943) is not negligible and also small quantum corrections are required (Yarnell *et al* 1973).

Thus the structure, or $g(r)$, of liquid argon is well understood.

The structure of liquid neon has been measured by neutron diffraction by Henshaw (1958), by x-ray diffraction by Stirpe and Thompson (1962) and by neutron diffraction by de Graaf and Mozer (1971). The last-named results are surely the most accurate. They measured the liquid at 35.05 K for three pressures, 21.4, 79.0 and 140.0 atm. We use their results for $g(r)$ for 21.4 atm for which the liquid number density is 0.03169 Å^{-3}. The results are conveniently tabulated by Raveché and Mountain (1972) and are shown (circled dots) on figures 1 and 2. They extend to unusually high values of r and this is of special interest to us here.

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De Graaf and Mozer tested their results for $g(r)$ for liquid neon and appear to conclude that they do not correspond to an effective pair-interaction potential of LJ form. This is anomalous because in other respects neon 'corresponds' to argon when suitably scaled. For instance, Hansen and Weis (1969) have shown that the thermodynamic properties of liquid neon are given very well by the LJ potential, when quantum corrections to order $\hbar^2$ are included. They found moreover that the LJ parameters for the best fit to the liquid properties were those already found to fit the solid by Brown (1966) and by Hansen (1968). These are $\varepsilon/kK = 36.76$ and $\sigma = 2.786$ Å, afterwards referred to as the solid/liquid or S/L values, rather than $\varepsilon/kK = 35.6$ and $\sigma = 2.740$ Å, as found for gas properties (de Boer and Michels 1938), afterwards referred to as the gas, or G, values.

However, de Graaf and Mozer did not include quantum corrections in their analysis of $g(r)$ and did not explicitly consider the fit for large values of r.

It seems to be generally felt that quantum corrections to $g(r)$ are very small for liquid argon. This is stated to be so by Yarnell *et al* (1973) and by Barker and Henderson (1976), but no quantitative results have ever been given. Also it is generally thought that the corrections are moderate for liquid neon and large for liquid helium. These assertions have been quantitatively confirmed only recently and will be reported in detail elsewhere (Powles and Abascal 1983).

By use of the effective potential to order $\hbar^2$ (Mayer and Band 1947), using perturbation theory and the discrete representation of statistical mechanics (Barker and Henderson 1967), with some approximations and considerable help from computer simulations, Powles and Abascal (1983) have estimated the quantum corrections to $g(r)$ for liquid neon for the LJ potential. The correction is given on figure 1, labelled C. Also

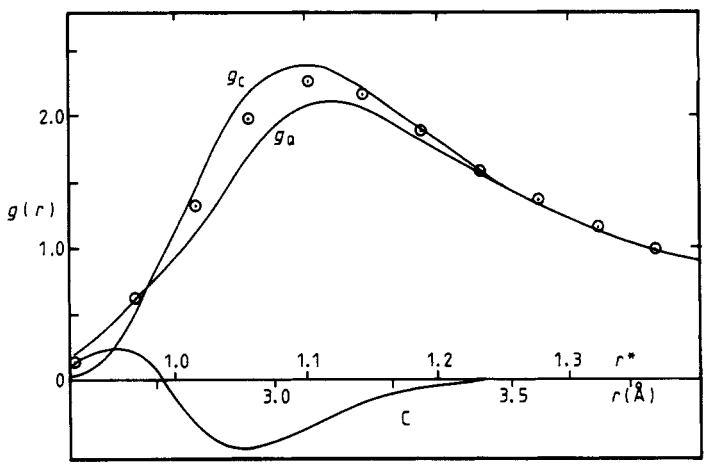

Figure 1. Pair-distribution functions for liquid neon. Circled dots are experimental results for 35.05 K and 21.4 atm (de Graaf and Mozer 1971). g_c is the classical result for a Lennard-Jones 12–6 pair-interaction potential with $\varepsilon/kK = 36.76$ and $\sigma = 2.786$ Å. The quantum correction from Powles and Abascal (1983) is labelled C. The corresponding quantum-corrected distribution function is labelled g_Q.

shown is the classical LJ $g(r)$, labelled $g_c(r)$ (Verlet 1968, interpolated to $T^* = 0.953$ and $\rho^* = 0.685$), and the quantum-corrected $g(r)$, labelled $g_Q(r)$. These are for the S/L values of ε and σ given above.

It was essentially the discrepancy between the result g_c and the experimental points in figure 1 which led de Graaf and Mozer to reject the LJ potential. The preliminary results of Powles and Abascal still do not reproduce the experimental results as well as might be hoped in that the amplitude of the first peak is some 7% too low. However, the quantum correction has moved the first peak up in r by almost the right amount to agree with experiment. Moreover, the agreement of g_Q and experiment at low values of r shows that the theory accounts well for the quantum repulsive-barrier-penetration effect.

The point we wish to make here particularly is that, while the magnitude of the quantum correction may not be quite right, it is surely safe to conclude that the quantum correction to $g(r)$ is quite negligible for, say, $r^* > 1.3$ or $r > 3.6$ Å. This conclusion only depend on the perturbation expansion and the expansion to order $\hbar^2$ being reasonable, as is surely the case for liquid neon.

The fact that the quantum corrections to $g(r)$ are small for large r appears not to have been noted previously.

We therefore compare the classical LJ result, $g_c(r)$, or more demandingly, $r(g_c(r) - 1)$, with the experimental result for $r > 3.6$ Å and this is shown in figure 2.

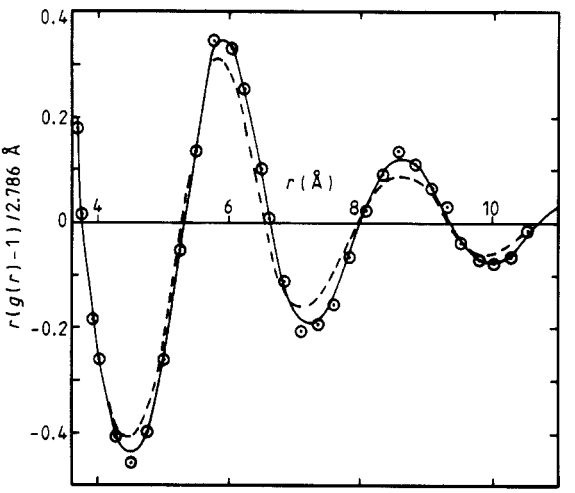

Figure 2. A comparison of the experimental values of $r\{g(r) - 1\}$ (circled dots) with the classical theoretical result for a L-J potential, for $r > 3.6$ Å. The full curve is for the solid/liquid values of ε and σ, given in the caption to figure 1. The broken curve is for the gas values, $\varepsilon/kK = 35.6$ and $\sigma = 2.740$ Å.

The agreement with experiment is excellent. Indeed it can even be seen that the S/L values of ε and σ give a markedly better fit than the G values. Thus the structural results are now in perfect accord with the thermodynamic results for the solid and liquid and correspond to an effective pair-potential of Lennard-Jones 12–6 form.

The structure of liquid neon is not therefore anomalous. It falls into line as one of the rare gas liquids, as one would indeed expect.

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