A UNIQUENESS THEOREM FOR FLUID PAIR CORRELATION FUNCTIONS

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It is shown that, for quantum and classical fluids with only pairwise interactions, and under given conditions of temperature and density, the pair potential $v(r)$ which gives rise to a given radial distribution function $g(r)$ is unique up to a constant.

Attempts are often made to deduce information on molecular interactions in the liquid state by analysis of the measured radial distribution function $g(r)$ [e.g. 1]. Under the assumption of only pairwise interactions, this work proceeds, for instance, by solution of one of the common integral equations or by fitting the measured data with computer simulation results. It is usually assumed that, once a pair potential $v(r)$ is found which reproduces a given $g(r)$, it is the only one which will do so. This unique relation is manifest in the integral equations, but, so far as this author is aware, has not been demonstrated beyong the context of these approximate treatments. In this note, we offer a general proof. In particular, we demonstrate as a rigorous consequence of statistical mechanics in both the quantum and classical cases that, for a given system under given conditions of temperature and density, two pair potentials which give rise to the same $g(r)$ cannot differ by more than a constant. The proof of this results is a straightforward adaptation of an argument given for the single particle density by Hohenberg and Kohn [2] and Mermin [3].

We consider a system of N identical particles in a volume V in thermal equilibrium at temperature T. Thermal averages are taken in a canonical ensemble. There are no external forces, and the particles are taken to interact in pairs through a potential $v(r)$. The system Hamiltonian is therefore

$$H = \sum_i \frac{p_i^2}{2M} + \tfrac{1}{2} \sum_{i \neq j} v(r_i - r_j) , \qquad (1)$$

where r_i denotes the position of the ith particle. The two particles distribution function $n_2(r, r')$ gives the probability density for finding one particle at r and another simultaneously at r' [e.g. 4]. In terms of this function, the thermal average of the second term in (1) is

$$\langle \tfrac{1}{2} \sum_{i \neq j} v(r_i - r_j) \rangle = \tfrac{1}{2} \int dr\, dr'\, v(r - r')\, n_2(r, r') . \qquad (2)$$

In the thermodynamic limit, n_2 becomes $n^2 g(r)$, where n is the average density, and $g(r)$ is the radial distribution function.

The uniqueness theorem follows from an inequality for the Helmholtz free energy. We consider two systems under identical conditions of temperature, volume and density, and described respectively by Hamiltonians H_1 and H_2. Then, in both classical and quantum statistics, the corresponding free energies F_1 and F_2 are related by [5]

$$F_2 \leqslant F_1 + \langle H_2 - H_1 \rangle_1 , \qquad (3)$$

where $\langle \ \rangle_1$ denotes averaging with the distribution appropriate to H_1. The important point in the following argument is that the *equality* holds in (3), at finite temperatures, if and only if $H_2 - H_1$ is independent of all coordinates and momenta *.

We now consider two systems which are identical in every respect except that the pair potential in one is $v(r)$ and in the other is $v'(r)$. The corresponding two particle functions are n_2 and n_2'. The uniqueness theorem asserts that, if $n_2(r, r') = n_2'(r, r')$ for all r and r', then v and v' can differ by no more than a constant. To prove this result, we suppose first that v and v' differ by more than a constant. Then, for all finite T, the condition for equality in (3) is violated,

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* At $T = 0$, the uniqueness theorem can be proved using the well known variational property of the ground state energy [e.g. 2]. In the limit as $T \to \infty$, equality may be approached even if $H_2 - H_1$ is not constant.

and we must have

$$F < F' + \langle H - H' \rangle' \, ,$$

or

$$F < F' + \tfrac{1}{2} \int \mathrm{d}r \, \mathrm{d}r' \, [v(r - r') - v'(r - r')] \, n_2'(r, r') \, , \quad (4)$$

where use has been made of (2). This argument may be repeated with primed and unprimed systems interchanged, giving

$$F' < F + \tfrac{1}{2} \int \mathrm{d}r \, \mathrm{d}r' \, [v'(r - r') - v(r - r')] \, n_2(r, r') \, . \quad (5)$$

If we now suppose that $n_2(r, r') = n_2'(r, r')$ for all r and r', addition of (4) and (5) yields $0 < 0$. Thus, two pair potentials which differ by more than a constant cannot give rise to the same n_2, and this is equivalent to the stated result. We note that this argument is independent of whether quantum or classical statistics is used.

We emphasize that this argument does not prove the existence of a solution for $v(r)$ given n_2, but only the uniqueness of the solution once it has been found. Its chief value perhaps is that it provides the justification for solution for $v(r)$ by trial and error.

We note, finally, that the argument has not required the r_i to represent only spatial coordinates. These could represent orientational coordinates as well, so that the theorem is equally valid in application to the angular pair correlation function of molecular liquids [e.g. 6].

References

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[5] The proof of (3) in the quantum case is attributed to Bogoliubov (see H. Falk, noted below), and in the classical case of Gibbs (Elementary principles of statistical mechanics (Dover Publications, New York 1960) Theorem III, page 131.). See also T. Lukes and T. Jones, J. Phys. A1 (1968) 29;
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