The Henderson Theorem

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In 1974 R. L. Henderson [Physics Letters **A49**, 197-198 (1974)] proved that for classical or quantum fluids with only pairwise interactions the pair potential $u(r)$ which gives rise to a given radial distribution function $g(r)$ is unique up to a constant. In this brief note Henderson's short proof is presented, including some notes on the crucial Gibbs inequality.

A (classical or quantum) system described by the Hamiltonian

$$H \ = \ \sum_i \frac{p_i^2}{2m} + \frac{1}{2}\sum_{i\neq j} u(|\boldsymbol{r}_i - \boldsymbol{r}_j|) \tag{1}$$

will give rise to a unique pair correlation function $g(r)$ (in the canonical ensemble). Henderson's theorem asserts that the reverse is also true: Two systems, which have a Hamiltonian of the form (1) and which feature the same $g(r)$ have pair potentials which differ at most by a trivial constant.

This uniqueness theorem follows as a beautiful application of the Gibbs-Bogoliubov inequality. For two systems with Hamiltonian H_1 and H_2 the following inequality holds for their free energies:

$$F_2 \ \leq \ F_1 + \langle H_2 - H_1\rangle_1 \ . \tag{2}$$

where $\langle\cdots\rangle_1$ denotes the (canonical) average appropriate for H_1. The key point is that *equality* holds if and only if $H_2 - H_1$ is independent of all degrees of freedom, which implies that the pair potentials can differ only by a constant. See the Appendix for a proof of this inequality.

Consider now two systems which are identical in all respects except that the pair potential in one is u_1 and the pair potential in the other is u_2. The corresponding two particle distributions are g_1 and g_2. The uniqueness theorem asserts that if $g_1 \equiv g_2$, then $u_1 - u_2$ is a constant. Now, if $u_1 - u_2$ differ by more than just a constant, the same holds for $H_2 - H_1$, and thus equality in (2) cannot hold, i.e., we have $F_2 < F_1 + \langle H_2 - H_1\rangle_1$. Or, more explicitly,

$$f_2 \ < \ f_1 + \frac{1}{2}n\int \mathrm{d}^3r\big[u_2(r) - u_1(r)\big]g_1(r) \ , \tag{3}$$

where the f_i are the free energies per particle and n is the average particle density. The above argument can be repeated with system 1 and 2 interchanged, which leads to

$$f_1 \ < \ f_2 + \frac{1}{2}n\int \mathrm{d}^3r\big[u_1(r) - u_2(r)\big]g_2(r) \ . \tag{4}$$

If we now use the fact that $g_1 \equiv g_2$ and add the inequalities (3) and (4), we obtain the contradiction $0 < 0$. This proves that the initial assumption that u_1 and u_2 differ by more than a constant must be wrong.

It must be noted that the above line of reasoning guarantees *uniqueness*, but not *existence* of a pair potential.

Appendix: The Gibbs inequality

Given two probability densities w_1 and w_2, the following inequality holds:

$$\mathrm{Tr}\Big[w_1 \log w_2\Big] \ \leq \ \mathrm{Tr}\Big[w_1\log w_1\Big] \ , \tag{5}$$

where the trace "Tr" means the integral over the probability space. The proof follows very easily from the elementary inequality $\log(x) \leq x - 1$:

$$\begin{aligned} \mathrm{Tr}\Big[w_1\log w_2\Big] - \mathrm{Tr}\Big[w_1\log w_1\Big] \ &= \ \mathrm{Tr}\Big[w_1 \log\frac{w_2}{w_1}\Big] \\ \leq \ \mathrm{Tr}\Big[w_1\big(\frac{w_2}{w_1} - 1\big)\Big] \ &= \ \mathrm{Tr}\, w_2 - \mathrm{Tr}\, w_1 \ = \ 0 \ . \end{aligned} \tag{6}$$

The same inequality holds if the w_i are not probability distributions but state operators, *i.e.*, self adjoint positive operators on some Hilbert space with trace 1. The proof then follows by using the spectral representation of the operators $\hat{w}_i$. Both in the classical and the quantum case the proof shows that equality only holds if $w_1 = w_2$ (Lebesgue almost everywhere in the classical case).

A particularly neat application follows if we choose as w_1 and w_2 the canonical states corresponding to Hamiltonians H_1 and H_2, *i.e.*, $w_i := \exp\{-\beta H_i\}/\mathrm{Tr}\exp\{-\beta H_i\}$:

$$\begin{aligned} \mathrm{Tr}\Big[w_1\big(-\beta H_2 - \log\mathrm{Tr}\,\mathrm{e}^{-\beta H_2}\big)\Big] \ &\leq \ \mathrm{Tr}\Big[W_1\log W_1\Big] \\ -\langle H_2\rangle_1 - k_\mathrm{B}T \ \log\mathrm{Tr}\,\mathrm{e}^{-\beta H_2} \ &\leq \ -TS_1 \ , \end{aligned}$$

and thus

$$F_2 \ \leq \ \langle H_2\rangle_1 - TS_1 \ . \tag{7}$$

Since we of course also have $F_1 = \langle H_1\rangle_1 - TS_1$, elimination of TS_1 between these two expressions immediately gives the inequality (2).