A generalization of Henderson's theorem

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Theorem 1. *Suppose the Hamiltonian H of a system in the canonical ensemble at ρ, T is given by a linear sum or integral*

$$H = \sum_i K_i f_i \left(\{\vec{r}\}\right) \tag{1}$$

where K_i are real numbers, f_i are non-constant functions of particle coordinates $\{\vec{r}\}$.

If for two equilibrium systems at ρ, T, $\langle f_i \rangle = \langle f_i' \rangle$ for all i, where $\langle\rangle$ is ensemble average over the equilibrium distribution of configurations (or volume average if ergodic), then we have $K_i = K_i'$ for all i.

For example, for the LJ 6-12 potential, $i = 1, 2$, $\langle f_1 \rangle = \langle \frac{1}{r^{12}} \rangle$, $\langle f_2 \rangle = \langle \frac{1}{r^6} \rangle$. The generalized Henderson's theorem states that if two LJ 6-12 potentials give the same $\langle \frac{1}{r^{12}} \rangle$ and $\langle \frac{1}{r^6} \rangle$ under equilibrium, then their parameters must be the same.

For general pairwise additive potentials, the sum in eqn. 1 is an integral over r. $\langle f(r) \rangle$ is surface area of a n-dimensional sphere with radius r multiplied by $g_2(r)$, and $K(r)$ is simply the pair potential $U(r)$. Then we recover the original Henderson's theorem.

The generality of the theorem is that the potential doesn't have to be pairwise additive, because f_i can be any function of particle coordinates. Also, $\langle f_i \rangle$ can be any ensemble average of a "feature" of the configuration. It doesn't have to be n-point distribution function.

Proof. The proof is exactly analogous to Henderson's proof about radial distribution functions.

Let H_1, H_2 be two potentials that can be written as eqn. 1 with the same forms of f_i, but possibly different K_i.

Let $\langle\rangle_1$ and $\langle\rangle_2$ be averages over equilibrium distributions of configurations under potentials H_1, H_2, respectively. Then for free energies,

$$\langle G_2 \rangle_2 \leq \langle G_2 \rangle_1 \tag{2}$$

Here, equality holds if and only if equilibrium distributions 1 and 2 are the same, therefore the potentials H_1, H_2 differ by no more than a constant.

From the equation above,

$$\langle H_2 \rangle_2 - TS_2 \leq \langle H_2 \rangle_1 - TS_1 \tag{3}$$

where S is the entropy.

If $\langle f_i \rangle_1 = \langle f_i \rangle_2$ for all i, $\langle H_2 \rangle_1 = \langle H_2 \rangle_2$. Then at positive T, $S_2 \geq S_1$.

By symmetry, $S_2 \leq S_1$. Therefore $S_1 = S_2$.

So the equality in eqn. 2 holds, and the potentials differ by no more than a constant. Since both potentials can be written has eqn. 1 where f_i are non-constant, we have same K_i for both H_1, H_2. □