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LETTER TO THE EDITOR

On a recent letter by Lesk

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Abstract. A recent letter by Lesk purporting to calculate the free energy of a hard-sphere gas is shown to be incorrect.

In a recent letter, Lesk (1974) gives as a closed-form solution to the hard-sphere gas partition function

$$Q(N, V) = V_0^N \frac{\Gamma((V/V_0)+1)}{\Gamma((V/V_0)+1-N)},$$

which may be rewritten as

$$Q(N, V) = \frac{1}{N!} \prod_{k=0}^{N-1} (V-kV_0),$$

where the missing $1/N!$ has been included. Apart from this missing term, simple geometrical considerations immediately show that the result is false for $N > 3$. It is however true in the zero-density limit, and represents a weak upper bound on the true partition function. It does not reproduce the known correct result in one dimension.

The canonical partition function for $N+1$ particles can be written as

$$Q(N+1, V) = \frac{1}{(N+1)!} \int \mathrm{d}r_{N+1} \int \cdots \int \mathrm{d}r_N \cdots \mathrm{d}r_1 \prod_{\substack{i=1\\ j=1\\ i<j}}^{N} \theta(r_{ij}) \prod_{i=1}^{N} \theta(r_{i,N+1})$$

with

$$\theta(r) = \begin{cases} 0 & \text{if } r < r_0 \\ 1 & \text{otherwise.} \end{cases}$$

Lesk claims that this can be rewritten as

$$Q(N+1, V) = \frac{Q(N, V)}{N+1} \int_R \mathrm{d}r_{N+1}$$

where the region of space $R(r_1 \ldots r_N)$ 'consists of a disjoint set of N balls, each of volume V_0, surrounding each of the first N particles'. This result is not true, since the region of space $R(r_1, \ldots, r_N)$ is very complex, and is given not only by the volume surrounding N balls, but also by certain complex volumes generated by the excluded regions of space in certain configurations. These volumes depend on the positions of the other N balls, and so the integral cannot be decoupled in the manner claimed.

For a one-dimensional system, an approach along these lines can be employed (see for example Thompson 1972), but it does not generalize to higher dimensions. In one dimension we can write

$$Q(N, V) = \int_{(N-1)r}^{V} \mathrm{d}r_N \int_{(N-2)r}^{r_N - r} \mathrm{d}r_{N-1} \ldots \int_{r}^{r_3 - r} \mathrm{d}r_2 \int_{0}^{r_2 - r} \mathrm{d}r_1$$

which on substituting $v = V-(N-1)r$ gives $Q(N, V) = v^N/N!$. Unfortunately, the solution to the long outstanding hard-sphere problem is just not that easy.

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References

Lesk A M 1974 *J. Phys. A: Math., Nucl. Gen.* 7 L146–8
Thompson C J 1972 *Mathematical Statistical Mechanics* (New York: Macmillan) pp 81–4