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1974 J. Phys. A: Math. Nucl. Gen. 7 L146

(http://iopscience.iop.org/0301-0015/7/13/002)

J. Phys. A: Math., Nucl. Gen., Vol. 7, No. 13, 1974. Printed in Great Britain. © 1974

LETTER TO THE EDITOR

On the recursive computation of the free energy of the hard-sphere gas

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Received 2 July 1974

Abstract. A modification of the recently published derivation of an expression for the free energy of a hard-sphere gas permits its evaluation in closed form.

Clippe and Evrard (1974) have recently published a method for approximating the free energy of a hard-sphere gas. The purpose of this letter is to show that by a modification of their derivation, an expression for this quantity is available in closed form.

Clippe and Evrard addressed themselves to the problem of evaluating

$$-A/kT = \ln Q(N, V) = \int \ldots \int \mathrm{d}r_1 \ldots \mathrm{d}r_N \exp(-\beta u)$$

where

$$u = \sum_{i \neq j} u(r_{ij})$$

and

$$u(r_{ij}) = \begin{cases} \infty & \text{if } r_{ij} < r_0 \\ 0 & \text{if } r_{ij} > r_0. \end{cases}$$

They point out that

$$\exp(-\beta u) = \prod_{i,j} \theta(r_{ij})$$

where,

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

and develop an approximate recursion relation for $Q(N, V)$ as a function of N for fixed V.

Provided that the total accessible volume V is greater than the volume occupied by the particles themselves, an exact recursion relation may be derived. For, comparing

$$Q(N, V) = \int \ldots \int \mathrm{d}r_1 \ldots \mathrm{d}r_N \prod_{\substack{i=1 \\ j=1 \\ i \neq j}}^{N} \theta(r_{ij})$$

with

$$Q(N+1,V)=\int\ldots\int \mathrm{d}r_1\ldots\mathrm{d}r_{N+1}\prod_{\substack{i=1\\j=1\\i\neq j}}^{N+1}\theta(r_{ij}),$$

the latter may be written in the form

$$Q(N+1,V)=\int \mathrm{d}r_{N+1}\int\ldots\int \mathrm{d}r_1\ldots\mathrm{d}r_N\prod_{\substack{i=1\\j=1\\i\neq j}}^{N}\theta(r_{ij})\prod_{i=1}^{N}\theta(r_{i,N+1}).$$

The product of those factors that contain coordinates of particle $N+1$, namely $\theta(r_{i,N+1})$, vanishes except in a region of space $R(r_1,\ldots,r_N)$ that consists of a disjoint set of N balls, each of volume V_0, surrounding each of the first N particles. Within the region R it is equal to 1. The integral $Q(N+1,V)$ may therefore be written:

$$Q(N+1,V)=\int_R \mathrm{d}r_{N+1}\left(\int_{\substack{\text{all}\\\text{space}}}\ldots\int \mathrm{d}r_1\ldots\mathrm{d}r_N\prod_{\substack{i=1\\j=1\\i\neq j}}^{N}\theta(r_{ij})\right).$$

But now the integrand, in large parentheses, is independent of r_{N+1}, and is equal simply to $Q(N,V)$.

Therefore

$$Q(N+1,V)=(V-NV_0)Q(N,V)$$

where $V-NV_0$ is the volume of the region R. This is the desired recursion relation.

Because $Q(1,V)=V$, the result is

$$Q(N,V)=\prod_{i=1}^{N}[V-(i-1)V_0]=V_0^N\frac{\Gamma((V/V_0)+1)}{\Gamma((V/V_0)+1-N)}.$$

That the latter expression is non-singular follows from the assumption that there is really room for all the particles.

$$-A/kT=\ln Q(N,V)=\ln\prod_{i=1}^{N}[V-(i-1)V_0]$$

$$=\ln\left(V_0^N\frac{\Gamma((V/V_0)+1)}{\Gamma((V/V_0)+1-N)}\right).$$

In the low density limit it is appropriate to rewrite this result as

$$-A/kT=\sum_{i=1}^{N}\ln\{V[1-(i-1)(V_0/V)]\}=N\ln V+\sum_{i=1}^{N}\ln[1-(i-1)(V_0/V)].$$

These equations are still exact. However, introducing the approximation $\ln(1-\epsilon)\simeq -\epsilon$

$$\lim_{(NV_0/V)\to 0}(-A/kT)=N\ln V-\sum_{i=1}^{N}(i-1)(V_0/V)$$

$$=N\ln V-[\tfrac{1}{2}N(N-1)](V_0/V)$$

$$\simeq N\{\ln V+\ln[1-\tfrac{1}{2}(N-1)(V_0/V)]\}$$

$$=N\ln[V-\tfrac{1}{2}(N-1)V_0]$$

which is equivalent to the van der Waals approximation (see Clippe and Evrard 1974, equation (11)) whenever $N-1 \simeq N$.

Work supported by research grant GJ-35327 from the US National Science Foundation.

References

Clippe P and Evrard R 1974 *J. Phys.* A: *Math., Nucl. Gen.* **7** L89–92