LETTER TO THE EDITOR

A new analytical approach to the determination of the hard-sphere gas free energy

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Abstract. A recurrence method is developed to derive a partial differential equation for the logarithm of the configurational integral of a hard-sphere gas. The free energy follows immediately, while comparison of analytical results to experimental data (on virtual hard-sphere gases like argon and xenon) gives quite remarkable precision.

The excess free energy A of a gas of N molecules in a volume V and at a temperature T is related to the configuration integral Q by the well known relation

$$-A/kT = \ln Q(N, V) \tag{1}$$

where $Q(N, V)$ is defined by

$$Q(N, V) = \int \ldots \int dr_1 \ldots dr_N \exp(-\beta u). \tag{2}$$

In the case of the hard-sphere gas, u is a sum of hard-sphere pair potentials

$$u(r) = \sum_{i,j} u(r_{ij}). \tag{3}$$

Here r_{ij} is the distance between the centres of the spheres i and j, and $u(r_{ij})$ is defined by

$$u(r_{ij}) = \begin{cases} \infty & \text{if } r_{ij} < r_0 \\ 0 & \text{if } r_{ij} > r_0 \end{cases} \tag{4}$$

where r_0 is twice the hard-sphere radius. Therefore, the factor $\exp(-\beta u)$, ie the hard-sphere distribution function, appears as the product of cut-off functions

$$\exp(-\beta u) = \prod_{i,j} \theta(r_{ij}). \tag{5}$$

By definition

$$\theta(r) = \begin{cases} 0 & \text{if } r < r_0 \\ 1 & \text{if } r > r_0. \end{cases} \tag{6}$$

Although the hard-sphere gas is a fundamental problem in statistical mechanics, the solutions proposed up to now do not seem entirely satisfactory (Rice and Gray 1965). Historically, the problem has been primarily tackled by means of the integral

equations method, the results of which are still unsatisfactory at low temperature and high density (Levesque 1966). Other mathematical approaches, like molecular dynamics and Monte Carlo methods (Rosenbluth and Rosenbluth 1954, Alder and Wainwright 1957) although leading to 'exact' results do not however bring much insight into the physical problem.

Here we propose a new approach (Clippe 1973) which leads to an approximate but, we hope, illuminating solution, besides being a source of possible generalizations. This approach is essentially based upon a partial differential equation obtained by the following recurrence procedure.

It is clear that adding an extra molecule to the gas while keeping the initial volume V unchanged imposes a spatial restriction on the volume available to the first N molecules. It is then possible to calculate the new configuration integral $Q(N+1, V)$ in the following way. Let us first suppose that the extra molecule is at a fixed position r. Then, the result of the integration over the N first molecules is the configuration integral for a gas of N molecules, but in a volume now reduced to $V - V_0$, where the quantity

$$V_0 = \tfrac{4}{3} \pi r_0^3$$

is called the exclusion volume of a hard sphere, ie eight times its volume. Obviously, V_0 is much smaller than V.

In a second step, one must integrate over the position of the extra molecule, which leads to a factor V, so that

$$Q(N+1, V) = VQ(N, V-V_0). \tag{7}$$

In fact this result is approximate, since excluding a volume V_0 with spherical shape and dimensions comparable to the molecular radius is not exactly equivalent to decreasing the volume of the gas by an uniform contraction. Indeed the possible configurations of the system are different in these two cases and the integration over these configurations can therefore give slightly different results.

Let us now suppose that dN molecules are added. One immediately obtains by recurrence

$$Q(N+\mathrm{d}N, V) \simeq V^{\mathrm{d}N}Q(N, V-\mathrm{d}NV_0) \tag{8}$$

if the dN added molecules are sufficiently far from each other in such a way that their exclusion volumes do not overlap. On the other hand, the expression

$$V(V-V_0)\ldots[V-(\mathrm{d}N-1)V_0]$$

appearing in (8) has been approximated by $V^{\mathrm{d}N}$, which is quite reasonable since V_0 is negligible compared to V.

After taking the logarithm of (8) and expanding in powers of dN, the linear terms lead to a partial differential equation, which is the corner stone of the new method:

$$1/\ln V \frac{\partial}{\partial N} f(N, V) + V_0/\ln V \frac{\partial}{\partial V} f(N, V) - 1 = 0 \tag{9}$$

where

$$f(N, V) = \ln \theta(N, V).$$

The equation (9) can be solved easily (Favard 1960). One obtains

$$f(N, V) = V/V_0 \ln V - V/V_0 + \psi(V - NV_0) \tag{10}$$

where $\psi(V - NV_0)$ is an arbitrary function to be determined from given 'boundary' condition. We impose that our solution be identical to the Van der Waals approximation in the limit of small densities ($NV_0 \ll V$). In the Van der Waals approximation

$$-A/kT = N \ln(V - \tfrac{1}{2}NV_0). \tag{11}$$

Hence $\ln Q(N, V)$ must tend to zero as $NV_0/2V$ tends to zero. Therefore

$$\psi(V - NV_0) = \frac{V - NV_0}{V} - \frac{V - NV_0}{V_0} \ln(V - NV_0) \tag{12}$$

substituting (12) and (10) into the definition of A leads to

$$-A/kT = N \ln V + N(1 - V/NV_0) \ln(1 - NV_0/V) - N. \tag{13}$$

This solution has no longer any meaning for densities high enough to have $NV_0/V \geqslant 1$. An analytical extension of the solution (13) can be found in replacing $(1 - NV_0/V)$ by its modulus $|1 - NV_0/V|$. Though this procedure is analytically not fully justified, practically it has been found to be valid when analysing experimental data (Clippe 1973).

The result (13) shows great similarity with that obtained for the free energy of a lattice gas (Coopersmith and Brout 1963). This is not surprising indeed, since a lattice gas of non-interacting molecules is subject to the restriction that at most one molecule can occupy a lattice site. Adding an extra molecule to the system reduces the volume available to the first N molecules by a quantity V_0, exactly as in our theory. Hence the above result (12), approximate in the case of a system of hard spheres, becomes exact for the lattice gas.

On the other hand, Zwanzig (1954) has expressed the free energy of a real gas as the sum of the free energy of a hard-sphere system plus perturbation terms. In such a manner, it is possible to evaluate this hard-sphere free energy from experimental data. The trick is to subtract any temperature dependent contribution from (1). We have applied this idea to argon (Clippe 1973). It appears that the hard-sphere gas contribution is indeed practically temperature independent. Detailed calculations will be published in a forthcoming publication.

The results are found in excellent agreement with the prediction of (13). A similar procedure (Clippe 1973) has also been used for the Van der Waals approximation (11). Although it gives good results, its precision is less remarkable. In table 1, the precision of the approximation proposed here is compared with that of the Van der Waals approximation for argon at densities up to 620 Am.

In conclusion, the recurrence method used to derive (8), when it is applied to the calculation of a gas of hard spheres, is in rather good agreement with experimental data in the region of moderate and high densities. It seems possible to extend the calculations

Table 1. Comparison between the present (CE) approximation and the Van der Waals approximation for the hard-sphere gas free energy deduced from experimental results for argon. The first row gives the maximum relative deviation (MRD) and the second the mean square relative deviation (MSD). The range of density goes from 1 Am to 620 Am, ie up to $NV_0 = 2V$ (1 Am = density of the gas at $T = 273 \cdot 16$ K and $p = 1$ atm).

A/kT	MRD	MSD
Van der Waals approximation	8 %	0·9 %
CE approximation	2·5 %	0·14 %

to higher densities. However this would require taking the overlap of the exclusion spheres into account.

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Note added in proof. The referee has kindly pointed out to us that our recurrence method had a precursor. When studying the canonical distribution of *quantum* gases, Landsberg (1961) has applied an iteration method to derive identities for Q_N. He then goes on to calculate the mean occupation numbers of bosons and fermions in a given quantum state, as well as a set of interesting inequalities. The situation is in fact more attractive since the complications arising from sphere overlaps are removed in such a case, ie r_0 tends to zero.

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