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Monte Carlo Calculation of Thermodynamic Properties of Simple Fluids

A METHOD of calculating properties of simple fluids by computer simulation appeared in 1953 (ref. 1). It entails the generation of large numbers of configurations of N fluid particles (represented by N triplets of co-ordinates) by random displacements of one particle at a time. The potential energy

$$\varphi = \sum_{i=1}^N \sum_{j>i}^N \varphi(r_{ij})$$

is calculated after each displacement; and, by rejecting appropriate fractions of all steps in which φ increases, one obtains a sequence of configurations which tends towards a Boltzmann distribution. The method has been applied, mainly by Wood *et al.*, to calculate the equation of state of hard-sphere fluids^{2,3}, the pressure, internal energy, specific heat and radial distribution function of argon (Lennard-Jones potential) at 55° C over a range of densities⁴ and the radial distribution function of liquid argon at -146.5° C (ref. 5).

The present extension of this method is designed to evaluate the classical configurational partition function

$$Z_c(V, T, N) = 1/N! \int \dots \int \exp(-\varphi/kT) dr \dots dr_N \quad (1)$$

and hence, in principle, all thermodynamic functions over a range V and T . $Z_c(V, T, N)$ can clearly be expressed in the form

$$VN/N! \int_{\varphi_{\min}}^{\varphi_{\max}} \exp(-\varphi/kT) f(\varphi) d\varphi \quad (2)$$

where $f(\varphi)d\varphi$ is the fraction of all accessible configurations for which the potential energy has a value between φ and $\varphi + d\varphi$.

Equation (2) can be evaluated as follows. By means of a bounded random walk among all accessible configurations the computer forms a histogram of the numbers of configurations with potential energy within intervals of small width ε . The n th entry is

$$F\left(\varphi_n - \frac{\varepsilon}{2}, \varphi_n + \frac{\varepsilon}{2}\right) \equiv F_n$$

The basic assumption is that—apart from a normalizing factor—this histogram converges statistically to $f(\varphi)$ as $\varepsilon \rightarrow 0$, and that, to a sufficient approximation,

$$Z_c(V, T, N) = C \sum_n \exp(-\varphi_n/kT) \cdot F_n \quad (3)$$

so that the partition function can be determined (apart from a constant factor) over a range of temperatures depending on the potential energy range covered by the histogram.

A second method of evaluation involves the formation of a sequence of Boltzmann-weighted configurations (com-

pare ref. 1). This is used to generate a histogram, of which the n th entry is

$$G_n(T) = \exp(-\varphi_n/kT) \cdot F_n$$

This determines equation (3) for the temperature T ; by means of re-weighting with Boltzmann factors corresponding to another temperature, that is

$$G_n(T') = G_n(T) \exp[-\varphi_n/k(1/T' - 1/T)]$$

equation (3) can be evaluated for a range of temperatures adjacent to T .

It is not practicable to determine the F_n -histogram for the entire range of potential energies; additional data are therefore required to calculate the change of the constant C in equation (3) with volume. To obtain these the virial

$$W = \sum_i r_i \cdot \nabla_i \varphi$$

as well as φ are calculated for each configuration and a table of mean virials \bar{W}_n corresponding to configurations within each potential energy interval

$$\left(\varphi_n - \frac{\varepsilon}{2}, \varphi_n + \frac{\varepsilon}{2}\right)$$

is formed. The weighted sum

$$W(T) = \sum_n W_n \exp(-\varphi_n/kT)$$

determines the virial and thus the pressure ($PV = RT - W/3$) for the same temperature range as Z_c . This method was suggested by I. R. McDonald. The isothermal variation of C can then be obtained by thermodynamic relationships, for example

$$A_c(V_2, T) - A_c(V_1, T) = - \int_{V_1}^{V_2} P dV; \quad (A_c = -kT \ln Z_c)$$

Table 1. COMPARISON OF CALCULATED AND EXPERIMENTAL RESULTS FOR GASEOUS ARGON

Molar volume (c.c.)	Temperature (°C)	Pressure (atm.)		Internal energy (cal. mole ⁻¹)		Specific heat (cal. mole ⁻¹ deg. ⁻¹)	
		calc.	exp. ⁶	calc.	exp. ⁶	calc.	exp. ⁶
70	0	294	326	-436	-487	0.36	0.44
	75	448	497	-462	-456	0.29	0.34
46.7	150	591	664	-443	-438	0.22	0.18
	0	548	622	-741	-714	0.56	0.66
35	75	877	948	-703	-668	0.46	0.54
	150	1,162	1,264	-673	-635	0.35	0.37
0	1,410	1,392	-954	-924	0.72	1.02	
	75	1,989	1,998	-892	-851	0.70	0.91
150	2,445	-	-850	-791	0.47	0.69	

Liquid argon, $T = 86^\circ \text{K}$.
 $P = 1 \text{ atm}$.

	Molar volume (c.c.)	Heat of vaporization (cal. mole ⁻¹)	Isothermal compressibility (cm ² dyne ⁻¹ × 10 ⁻¹⁰)
Calculated result	28.6	1,590	2.02
Experimental result ⁷	28.6	1,558	2.12

A selection of results obtained by I. R. McDonald for gaseous argon using the first method of evaluation given in this report ($N = 32$), and a few preliminary results for liquid argon calculated from the second method given ($N = 108$), are listed in Table 1. Calculations for condensed phases of interacting particles appear to be quite practicable. A full account of the work will be published elsewhere.

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