DETERMINATION OF THE FREE VOLUME 
AND THE ENTROPY BY A MONTE CARLO 
METHOD

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ABSTRACT

The configurational integral can in principle, though not in practice, be determined from the ratio of accepted to rejected moves \(\langle a_N(v)\rangle\) in the Monte Carlo method of Metropolis et al., if the moves consist of simultaneous random displacements of \(N\) particles uniformly distributed over the sample volume \(v\). In the usual Monte Carlo process only one particle at a time is displaced within a small volume. If this volume is suitably chosen \((v_p)\), the acceptance ratio \(\langle a_I(v_p)\rangle\) determines the mean free volume per particle \(v_f = v_p \langle a_I(v_p)\rangle\). Evidence is presented supporting the approximate validity of the relationship \(\langle a_N(v)\rangle = \langle a_I(v_p)\rangle^N\) which permits the evaluation of the configurational integral. The entropies calculated in this way for a system of 108 Lennard–Jones particles with parameters corresponding to argon, are in good agreement with the experimental values for solid and liquid argon. The results indicate that the full amount of the communal entropy appears on fusion.

In the well-known Monte Carlo (MC) method of Metropolis et al.\(^1\) certain many-dimensional integrals containing the Boltzmann factor as weighting function are evaluated by means of the following procedure: configurations of a system of \(N\) particles are generated by small random displacements of single particles; if \(r^N_{a+1} = r^N_a\) is the configuration after \(a\) moves and the next trial move leads to \(r^N_a\), then this move is rejected (by setting \(r^N_{a+1} = r^N_a\)) if and only if the difference between the potential energies \(\Phi(r^N_a) - \Phi(r^N_{a+1}) = \Delta \Phi > 0\) and \(\exp (-\Delta \Phi/kT) < \eta\), \(\eta\) being a number chosen at random between 0 and 1; otherwise the move is accepted (by setting \(r^N_{a+1} = r^N_a\)).

If in this process configurations were generated by simultaneous displacements of all \(N\) particles to random positions uniformly distributed over the sample volume \(v\), the configurational integral could in principle be evaluated from the mean acceptance ratio for the trial moves

\[
\frac{\int_0^1 \cdots \int_0^1 \exp \left[-\{\Phi(r^N_a) - \Phi_{\text{min.}}\}/kT\right] \, dr^N}{\int_0^1 \cdots \int_0^1 \, dr^N} = \frac{Q(NvT) \exp(\Phi_{\text{min.}}/kT)}{v^N} \] \[= \lim_{M \to \infty} \frac{\sum_{a=1}^M \exp \left[-\{\Phi(r^N_a) - \Phi_{\text{min.}}\}/kT\right]}{M} = \frac{\text{no. of accepted moves}}{\text{no. of attempted moves}} \]

\[= \langle a_N(v)\rangle \] \[(1)\]
Table 1. Comparison of the statistics of consecutive acceptances (runs) of MC moves with the corresponding statistics for independent events of equal probability, calculated with the formula
\[ f(M) = M(1 - p)p^a/(M - pU), \]
with \( p = \langle a_i(v_d) \rangle, \ v_d = (4\pi/3) R_d^3 \)

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Volume (cm³/mole)</th>
<th>M</th>
<th>Length of Run (a)</th>
<th>T</th>
<th>a</th>
<th>f_{obs}</th>
<th>f_{calc}</th>
</tr>
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<tbody>
<tr>
<td>50.0</td>
<td>24.24</td>
<td>20</td>
<td>N = 108</td>
<td>2</td>
<td>8</td>
<td>51375</td>
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T is temperature in °K.  
\( R_d \) is range of displacements in Å.  
\( V \) is volume in cm³/mole.  
\( N \) is number of particles.  
a is number of displacements accepted consecutively (length of run).  
f_{obs} and f_{calc} are the observed and calculated frequencies of the number of displacements accepted consecutively.
### Entropy by a Monte Carlo Method

<table>
<thead>
<tr>
<th>M = 12800</th>
<th>( R_d = 0.065 )</th>
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<tr>
<td>38 44 50</td>
<td>56 62 68</td>
</tr>
<tr>
<td>80 32 14</td>
<td>7 3 0</td>
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<td>71 30 12</td>
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<table>
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<tr>
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<tr>
<td>56 65 74</td>
<td>83 92 101</td>
</tr>
<tr>
<td>47 24 9 2</td>
<td>2 1 0</td>
</tr>
<tr>
<td>38 15 6 2</td>
<td>1 0 0</td>
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<td>83 92 101</td>
</tr>
<tr>
<td>12 4 2</td>
<td>1 0 0</td>
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<tr>
<td>13 4 1</td>
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<tr>
<td>29 15 5</td>
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<tr>
<td>35 12 4</td>
<td>1 0 0</td>
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</tr>
<tr>
<td>16 3</td>
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<tr>
<td>15 4</td>
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<td>7 3 3</td>
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<tr>
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</tr>
<tr>
<td>5 3 1</td>
<td>0 0 0</td>
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<tr>
<td>2 0 0</td>
<td>0 0 0</td>
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<table>
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<tr>
<th>M = 132800</th>
<th>( R_d = 2.07 )</th>
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<tr>
<td>M = 299008</td>
<td>( R_d = 2.07 )</td>
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<table>
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<td>134 156 178</td>
<td>200 222 244</td>
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<tr>
<td>31 11 8</td>
<td>5 2 1</td>
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<tr>
<td>24 10 4</td>
<td>2 1 0</td>
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<table>
<thead>
<tr>
<th>M = 145600</th>
<th>( R_d = R_p = 11.62 )</th>
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<tbody>
<tr>
<td>7 8 9</td>
<td>0 0 0</td>
</tr>
<tr>
<td>1 1 0</td>
<td>0 0 0</td>
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<tr>
<td>0 0 0</td>
<td>0 0 0</td>
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</tbody>
</table>

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(\Phi_{\text{min.}} \text{ is the lowest potential energy attained, and the angular bracket indicates an ensemble average; } v = L^2). This method is impracticable because the acceptance ratio \( \langle a_1(v_0) \rangle \) is too small and the numerical labour too great. Both difficulties are overcome in the usual process by the displacement of one particle at a time within a small volume \( v_d \ll v \), centred on the current position of the particle. The mean acceptance ratio, \( \langle a_1(v_d) \rangle \), has no physical significance here. When the range of attempted displacements is increased, the product \( v_d \langle a_1(v_d) \rangle \) increases up to a limiting value \( v_d^* \) such that for \( v_d \geq v_d^* \) the probability of acceptance of moves ending outside \( v_d \) it is virtually zero. For solids and liquids not too near the critical point, \( v_d < v/N \); for fluids of lower density even large displacements are accepted, i.e. \( v_d = v \). The acceptance ratio \( \langle a_1(v_D) \rangle \) is the MC estimate of the integral

\[
\langle \int \exp \left( -\Phi_1(r_1) - \Phi_{\text{min.}}^1 / kT \right) dr_1 \rangle_{N-1/v_D}^{N-1/v_D} \tag{2}
\]

where \( \Phi_1(r_1) \) and \( \Phi_{\text{min.}}^1 \) are the energy of particle 1 and its minimum value within \( v_D \), and the subscript \( N-1 \) indicates an average over all configurations of particles 2 to \( N \). The numerator of expression 2 can be interpreted as defining the free volume, \( v_f \).

The evaluation of the configurational integral is based on the proposition that, to a sufficient approximation,

\[
\langle a_4(v) \rangle = \langle a_1(v) \rangle^N \tag{3}
\]

First, it will be noted that the acceptance ratio for displacements over the whole volume \( v \) can be determined from

\[
v_d \langle a_1(v_d) \rangle = v \langle a_1(v) \rangle \tag{4}
\]

(for dense systems \( \langle a_1(v) \rangle \) is too small to be obtained directly.) Secondly, since the MC evaluation of a many-dimensional integral can be effected either by sampling the different dimensions simultaneously or consecutively (in cycles)

\[
\langle a_N(v) \rangle = \langle a_1(v) \rangle^N \tag{5}
\]

i.e. the mean probability of acceptance of a simultaneous displacement of \( N \) particles equals the joint probability of acceptance of \( N \) successive moves of one particle at a time. Thirdly, numerical experiments indicate that

\[
\langle a_1(v) \rangle = \langle a_1(v) \rangle^N \tag{6}
\]

The statistics of runs of acceptances in the MC process have been compared with the known statistics of runs of independent events. The results are summarized in Table 1. To obtain runs of length \( N (=108) \), it is necessary to reduce the range of displacements, \( R_d \), drastically. Alternatively, when \( R_d \) equals the radius of the spherical volume \( v_D \), only short runs are obtained. Under both these conditions the observed statistics agree closely with the statistics of independent events. Although this evidence for the validity of equation 6 is not entirely conclusive, it does indicate that the two sides of 6
Table 2. Data for the calculation of entropies and comparison with the entropy of argon

<table>
<thead>
<tr>
<th>No.</th>
<th>V cm$^3$ mol$^{-1}$</th>
<th>T $^\circ$K</th>
<th>M $10^3$</th>
<th>$\langle a_1(v_B) \rangle$</th>
<th>$N_0\psi_f$ cm$^3$ mol$^{-1}$</th>
<th>$R_D$ Å</th>
<th>$\langle \Phi \rangle - \Phi_{min,n}$ $NkT$ A A</th>
<th>$S_{MC}$ J K$^{-1}$ mol$^{-1}$</th>
<th>$S_{argon}$ J K$^{-1}$ mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. a, f</td>
<td>24.24 (c)</td>
<td>50.0</td>
<td>266</td>
<td>0.0240</td>
<td>0.092</td>
<td>1.18</td>
<td>0.166 0.535</td>
<td>22.6 24.6</td>
<td>23.3 d</td>
</tr>
<tr>
<td>2. b, f</td>
<td>24.24 (c)</td>
<td>86.3</td>
<td>176</td>
<td>0.00885</td>
<td>0.167</td>
<td>1.67</td>
<td>0.124</td>
<td>33.4</td>
<td>—</td>
</tr>
<tr>
<td>3. b, f</td>
<td>24.51 (c)</td>
<td>86.3</td>
<td>266</td>
<td>0.00891</td>
<td>0.171</td>
<td>1.97</td>
<td>0.147 0.757</td>
<td>34.5 38.2</td>
<td>38.8 d</td>
</tr>
<tr>
<td>4. b, g</td>
<td>28.48 (l)</td>
<td>97.0</td>
<td>398</td>
<td>0.0210</td>
<td>0.467</td>
<td>2.07</td>
<td>0.204 0.613</td>
<td>52.3 55.7</td>
<td>55.9 e</td>
</tr>
<tr>
<td>5. c, g</td>
<td>28.48 (l)</td>
<td>97.0</td>
<td>298</td>
<td>0.0214</td>
<td>0.476</td>
<td>2.07</td>
<td>0.180 0.631</td>
<td>51.4 55.8</td>
<td>55.9 e</td>
</tr>
<tr>
<td>6. b, g</td>
<td>29.69 (l)</td>
<td>97.0</td>
<td>266</td>
<td>0.0265</td>
<td>0.615</td>
<td>2.10</td>
<td>0.216</td>
<td>54.4</td>
<td>—</td>
</tr>
<tr>
<td>7. a, g</td>
<td>29.69 (l)</td>
<td>97.0</td>
<td>133</td>
<td>0.0281</td>
<td>0.652</td>
<td>2.10</td>
<td>0.229 0.595</td>
<td>55.0 57.6</td>
<td>58.4 e</td>
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<tr>
<td>8. b, g</td>
<td>28.48 (l)</td>
<td>108.0</td>
<td>266</td>
<td>0.0224</td>
<td>0.499</td>
<td>2.07</td>
<td>0.245 0.570</td>
<td>54.3 57.0</td>
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<td>9. a, g</td>
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<td>0.0804</td>
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<tr>
<td>11. b, h</td>
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<td>173.2</td>
<td>146</td>
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<td>297</td>
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<td>11.62</td>
<td>0.138 0.306</td>
<td>92.2 93.6</td>
<td>100.6 d</td>
</tr>
</tbody>
</table>

a: $N = 108$, LJ parameters $\varepsilon/k = 1172, \sigma = 3-405$ Å (ref. 3).
b: $N = 108$, LJ parameters $\varepsilon/k = 1198, \sigma = 3-405$ Å (ref. 7).
c: $N = 256$, LJ parameters $\varepsilon/k = 1198, \sigma = 3-405$ Å (ref. 7).
d: interpolated from data in ref. 8.
e: interpolated from data in ref. 9.
f: $C_a = 1$; $g: C = N^a/N^f$; $h: C = 1/N^f$.
A: method A; B: method B.
differ by less than an order of magnitude. A small error would have little effect on the entropy: since
\[
S/Nk = (1/N) \log (v^N \langle a_1(v) \rangle^N) + \text{other terms},
\]
a discrepancy by a factor ten between the two sides of 6 would (with \(N = 108\)) lead to an error of less than three per cent in the configurational entropy. The configurational partition function can therefore be written in the form
\[
Q = C \exp (-\Phi_{\text{min}}/kT) (v \langle a_1(v) \rangle)^N = C \exp (-\Phi_{\text{min}}/kT) v_f^N
\]
(7)
The value of \(C\) depends on the nature of the system: for localized particles (in solids), \(C = 1\); for dense fluids, when \(v_D < v/N\), \(C = N^N/N!\); for fluids of lower density, when \(v_D = v\), \(C = 1/N!\). There is a (not very extensive) region below the critical temperature where \(v/N < v_D < v\), when the present method is not applicable.

Entropies have been calculated with the formula
\[
S/Nk = (\langle \Phi \rangle - \Phi_{\text{min}})/NkT + 1.5 \{1 + \log(2\pi nkT/h^2)\}
+ (1/N) \log C + \log v_f
\]
(9)
for a model consisting of 108 (or 256) Lennard–Jones (12–6) particles with parameters corresponding to argon. As a first approximation \(\Phi_{\text{min}}\) was equated to the lowest total potential energy attained in the MC experiment (method A). Table 2 shows that this leads to entropies which are consistently by about eight per cent lower than the experimental values. This procedure is also unsatisfactory because \((\langle \Phi \rangle - \Phi_{\text{min}})/NkT\) estimated in this manner varies as \(N^{-1/2}\) instead of being an intensive quantity. This objection does not hold if \(\Phi_{\text{min}}\) is set equal to \((N/2) \langle \Phi_{\text{min}}^1 \rangle\) where \(\langle \Phi_{\text{min}}^1 \rangle\) is the mean value of the minimum of the potential energy of a particle in the field of the other particles. This step may be further justified as follows. Equation 2 can be written in the form
\[
\langle a_1(v) \rangle = \langle \int F_1(r_N) \, dr_1 \rangle_{N-1/v}
= \int \cdots \int (F_N/F_1) \, dr_2 \cdots dr_N \int F_1 \, dr_1 / \int \cdots \int (F_N/F_1) \, dr_2 \cdots dr_N \int \, dr_1
\]
where \(F_N = \exp \left(- (\Phi(r^N) - \Phi_{\text{min}})/kT \right)\). If equations 5 and 6 are to be valid, one must equate \(F_1\) to
\[
\exp \left(- (\Phi^1(r^N) - \Phi_{\text{min}}^1(r_2, \ldots, r_N))/2kT \right)
\]
and
\[
\Phi_{\text{min}} \text{ to } N \langle \Phi_{\text{min}}^1 \rangle/2,
\]
where
\[
\Phi^1(r^N) = \sum_{j=2}^{N} \varphi(|r_j - r_1|)
\]
and
\[
\Phi_{\text{min}}^1(r_2, \ldots, r_N) = \sum_{j=2}^{N} \varphi(|r_i - r_{1(\text{min})}(r_2, \ldots, r_N)|).
\]
\( \langle \Phi_{\text{min}} \rangle \) is determined from separate MC data. The values so obtained are in satisfactory agreement with the experimental entropies for solid and liquid argon (Table 2, method B). The persistent discrepancy for the gaseous V, T point is almost certainly due to the difficulty of determining \( \langle \Phi_{\text{min}} \rangle \) in this case.

In spite of this uncertainty, which calls for further investigation, the present methods has some advantages compared with the MC method employed in the impressive work of Hansen and Verlet. The statistical convergence of the acceptance ratio is excellent and the statistical error in the entropies after 2 to \( 3 \times 10^5 \) moves is of the order of one per cent. This compares very favourably with the accuracy of the MC estimate of pressure which is required in methods based on the integration of \( p \, dv \) along isotherms. Moreover, whereas the evaluation by the latter method of the free energy and entropy at one \( V, T \) point requires MC pressure data for \( \approx 12 \, V, T \) points, the proposed method requires data for one \( V, T \) point only. A similar saving of computational labour applies to MC calculations of the free energy of mixtures: these have been evaluated by integration with respect to continuously varying parameters along an isotherm. The most promising field of application of the present method is perhaps the calculation of the free volume and the entropy of different molecular and ionic species in mixtures.

REFERENCES