have evidently

$$\sum_X {}_mC_{m-X}\,{}_nC_X=(M+n)\,!/m!n!, \tag{6}$$

$$(1+y)^m=\sum_{X'} {}_mC_{m-X'}y^{m-X'}, \tag{7}$$

and

$$(1+y)^n=\sum_X {}_nC_X y^X. \tag{8}$$

We multiply Eq. (8), differentiated with respect to y, by Eq. (7) side by side, normalize by Eq. (6), and picking up the terms $X=X'$ we get the mean value as the coefficient of the $(m-1)$th term in the binomial expansion. Similarly the expression of σ^2 is derived when we use Eq. (8) differentiated two times and (7). After a transformation $t=(X-\bar{X})/\sigma$ is carried, a tedious calculation leads to

$${}_mC_{m-X}\,{}_nC_X=\frac{(m+n)\,!}{m!n!}\frac{1}{(2\pi\sigma^2)^{\frac{1}{2}}}\exp\left(\frac{-t^2}{2}\right). \tag{9}$$

Equation (9) is derived by the same method[2] that a binomial coefficient can be transformed to the asymptotic expression. Equation (9) may be rewritten in the variable X as follows

$${}_mC_{m-X}\,{}_nC_X=\frac{(m+n)\,!}{m!n!}\frac{1}{(2\pi\sigma^2)^{\frac{1}{2}}}\exp\left[-\frac{(X-\bar{X})^2}{2\sigma^2}\right]. \tag{10}$$

The sum of Eq. (4) can be carried after combining Eqs. (10) and (4) and replacing the sum by integration. The comparison of the sum of Eqs. (4) and (2) gives

$$h(m,n)=\left(\frac{(m+n)\,!}{m!n!}\right)^{1-z}(2\pi\sigma^2)^{z/4}\left[\frac{\pi}{z/4\sigma^2}\right]^{-\frac{1}{2}}. \tag{11}$$

Therefrom we have from Eqs. (11), (10), and (4)

$$g(m,n,X)=\frac{(m+n)\,!}{m!n!}\left(\frac{\pi}{z/4\sigma^2}\right)^{-\frac{1}{2}}\exp\left[-\frac{z(X-\bar{X})^2}{4\sigma^2}\right]. \tag{12}$$

At last substituting Eq. (12) into Eq. (1) we have the integration form of the configurational partition function:

$$Q=\int_{-\infty}^{\infty}g(m,n,X)\exp\left(\frac{m\chi_A+n\chi_B-Xw}{kT}\right)dX. \tag{13}$$

After integrating we have

$$Q=\exp\left(\frac{m\chi_A+n\chi_B}{kT}\right)\frac{(m+n)\,!}{m!n!}\exp\left(-\frac{\bar{X}w}{kT}+\frac{\sigma^2w^2}{zk^2T^2}\right). \tag{14}$$

Applications of this method will soon be published. The conventional concept of regular solutions is enlarged to a certain extent because of dependence of entropy on the temperature. The free energy derived by the present method in order–disorder problem agrees so far as the second term of w/kT with that obtained by Kirkwood in 1938.[3]

[1] R. H. Fowler and E. A. Guggenheim, *Statistical Thermodynamics* (Cambridge University Press, London, 1939).

[2] H. Margenau and G. M. Murphy, *The Mathematics of Physics and Chemistry* (D. Van Nostrand, Inc., New York, 1943), Chap. 12.

[3] J. G. Kirkwood, J. Chem. Phys. **6**, 70 (1938).

Calculated Scattering Cross Sections for He–He at Thermal Energies*

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THE He–He interaction potential has been the object of considerable theoretical attention.[1–3] Since further similar investigations are likely to produce only small refinements, it now appears worthwhile to carry

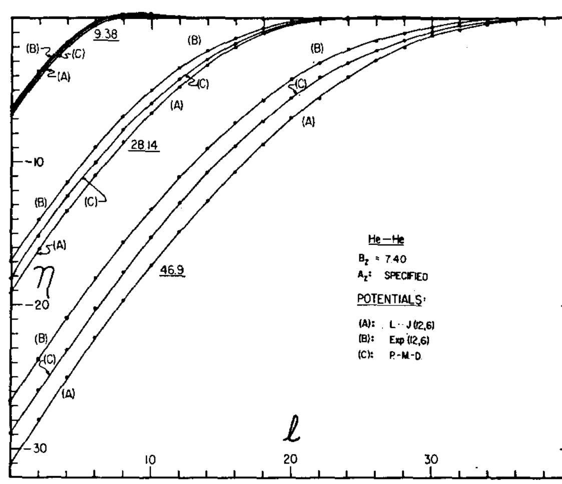

FIG. 1. Calculated phase shifts, $\eta_l(A_z)$ for the three indicated potentials (all with $\epsilon=1.40\times10^{-15}$ ergs, $r_m=2.973$ Å). Here $A_z=kr_m=9.36\times10^{-5}\,v(\text{cm sec}^{-1})$, $B_z=2\mu\epsilon r_m^2/\hbar^2=7.40$.

out computations of elastic scattering cross sections to allow prediction of (and comparison with) experimental results at thermal energies. We present a calculation[4] based on a potential constructed by joining Phillipson's[1] short-range repulsion via a Morse function to Dalgarno's[2] long-range attraction. Choosing a well depth $\epsilon=1.40\times10^{-15}$ ergs[3], r_m and connecting points are found by slope-matching; $r_m=2.973$ Å (cf. 2.91 Å[3],

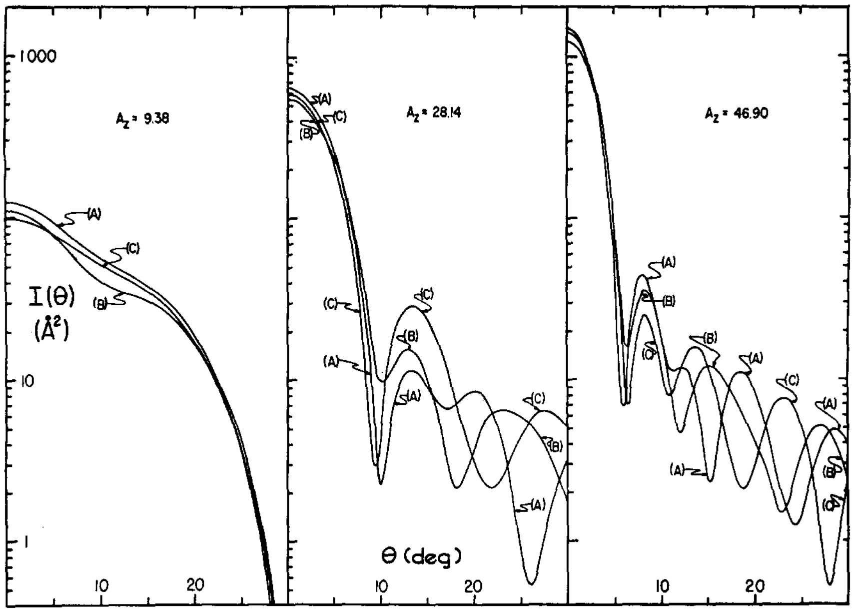

FIG. 2. Calculated differential cross sections $I(\theta)$ for each potential at three values of A_z.

3.05A[5]) and

$$
\begin{aligned}
V(r)[\mathrm{eV}(\text{Å})] &= 185.9\exp[-3.80r-0.025r^4]; \quad (0.5\leq r<1.00)\\
&= 8.739\times10^{-4}\{\exp[12.766(1-r/r_m)]\\
&\quad -2\exp[6.383(1-r/r_m)]\}; \quad (1.00\leq r<3.463)\\
&= -0.8689r^{-6}; \quad (r\geq 3.463). \qquad (1)
\end{aligned}
$$

Phases (Fig. 1) were computed by RKG integration.[4] Parallel calculations were performed for LJ(12, 6) and exp(12, 6) potentials of identical r_m, ϵ. Where comparison was possible they agreed with literature values.[6–10] Standard formulas for $I(\theta)$ and Q (Figs. 2, 3) were used, with double weighting of all phases (even l) appropriate for He^4–He^4 (spinless bosons). Calculated cross sections are proportional to r_m^2 but fairly insensitive to ϵ.

The existing measurements[11,12] are shown in Fig. 3. The experimental Q's are higher than the predicted values. Improvement in experimental accuracy, extension of the energy range and differential cross-section measurements are suggested.

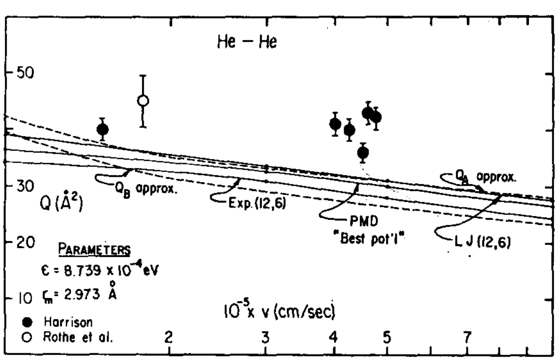

FIG. 3. Calculated vs observed total cross sections $Q(v)$ over the range $v=1-10\times10^5$ cm sec^{-1}. The curves labeled Q_A and Q_B [for the LJ (12, 6) and exp (12, 6) potentials, respectively] are estimates based on the "high-velocity approximation" [see R. B. Bernstein, J. Chem. Phys. **38**, 515 (1963)].

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[1] P. Phillipson, Phys. Rev. **125**, 1981 (1962).
[2] A. Dalgarno and A. E. Kingston, Proc. Phys. Soc. (London) **78**, 607 (1961).
[3] R. A. Buckingham, Trans. Faraday Soc. **54**, 453 (1958).
[4] For method, see R. B. Bernstein, J. Chem. Phys. **33**, 795 (1960).
[5] J. S. Rowlinson, Ann. Rept. Chem. Soc. **56**, 26 (1959).
[6] H. S. W. Massey and C. B. O. Mohr, Proc. Roy. Soc. (London) **A144**, 188 (1934).
[7] J. de Boer and A. Michels, Physica **6**, 409 (1939).
[8] R. A. Buckingham, J. Hamilton and H. S. W. Massey, Proc. Roy. Soc. (London) **A179**, 103 (1941).
[9] H. S. W. Massey and R. A. Buckingham, Proc. Roy. Soc. (London) **A168**, 378 (1938).
[10] O. Halpern and R. A. Buckingham, Phys. Rev. **98**, 1626 (1955).
[11] E. W. Rothe, L. L. Marino, R. H. Neynaber, P. K. Rol, and S. M. Trujillo, Phys. Rev. **126**, 598 (1962).
[12] H. Harrison, J. Chem. Phys. **37**, 1164 (1962).