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COLLISION INTEGRALS FOR THE EXPONENTIAL ATTRACTIVE POTENTIAL*

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ABSTRACT

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Collision integrals for the exponential attractive potential are calculated by accurate numerical integration. There are some unexpected differences from what had been expected by analogy with inverse power attractive potentials. Some implications of these results for the calculation of high-temperature gas transport properties are discussed.

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I. INTRODUCTION

Simple attractive or repulsive potentials are useful for calculations of the transport properties of gases, especially at high temperatures where the van der Waals forces are not important and the atomic interactions are governed by valence or exchange forces.[1,2] Single term inverse power laws have been a favorite representation of such potentials, partly because the evaluation of their transport collision integrals requires only a single set of quadratures. The numerical results available for inverse power attractive and repulsive potentials have been summarized and extended by Kihara, Taylor, and Hirschfelder.[3] However, it often happens that a single term exponential gives a better representation of the interaction than does an inverse power, but the evaluation of the collision integrals for an exponential potential requires a large amount of numerical quadrature. The collision integrals for the repulsive exponential have been accurately calculated by Monchick,[4] but the only results available for the attractive exponential are an estimate by Brokaw[5] based on a scaling analogy with attractive inverse powers.

The purpose of this paper is to report the calculation of the collision integrals for the exponential attractive potential by accurate numerical integration. Such a calculation is now comparatively easy because of the existence of an efficient computer program for the automatic calculation of collision integrals.[6]

Comparison of the results with those for inverse power attractive potentials and with Brokaw's estimates shows that the collision integrals for viscosity correlate well (i.e., Brokaw's estimates are reasonably accurate), but that the collision integrals for diffusion do not correlate well and in fact show a rather different temperature dependence. Some implications of these results for the calculation of high-temperature gas transport properties are discussed.

II. NUMERICAL CALCULATIONS

It is first necessary to decide on a condition at the origin for an attractive potential, inasmuch as different assumptions can lead to quite different collision integrals.[3] We chose the repulsive core condition, in which the potential has a small repulsive core at the origin to deflect outwards any trajectories of relative motion that reach the origin, since this is the most realistic model in the problems of physical interest. In the limit of a core of infinitesimal size, the exact nature of the repulsion is expected to be unimportant and can be chosen for mathematical convenience. The usual choice of a rigid-sphere core was impractical because of the discontinuity involved; a short-ranged exponential was therefore used, and the collision integrals for the attractive exponential were calculated as the low-temperature limits of the Morse potential,

$$\varphi(r) = \epsilon\left\{\exp\left[-2(C/\sigma)(r-r_e)\right] - 2\exp\left[-(C/\sigma)(r-r_e)\right]\right\} , \qquad (1)$$

where ϵ is the depth of the potential well, r_e its position, σ the

separation for which $\varphi(\sigma) = 0$, and C is a parameter which gives a measure of the width of the well, related to r_e and σ by the relation $C\left[(r_e/\sigma) - 1\right] = \ln 2$. If we write the attractive exponential in the form

$$\varphi(r) = -\varphi_0 \exp(-r/\rho), \tag{2}$$

then $\varphi_0 = 2\epsilon \exp(Cr_e/\sigma)$ and $\rho = \sigma/C$.

The conventional definition[7] of the reduced collision integrals $\Omega^{(\ell,s)*}$ to be equal to unity for rigid spheres of diameter σ, and to be functions of the reduced temperature $T^* = kT/\epsilon$, are inconvenient for exponential potentials,[4,5] and we have adopted the definitions[5]

$$J^{(\ell,s)} = (C^2/\alpha^2)\Omega^{(\ell,s)*}, \tag{3}$$

$$\alpha = \ln(\varphi_0/kT) = C - \ln(T^*/4). \tag{4}$$

The procedure was to pick a value of C and then evaluate $\Omega^{(\ell,s)*}$ by the previously described computer program[6] at successively lower values of T^* until the results appeared to be independent of the repulsive core. As a check the process was repeated with a new value of C. On converting all these results to a plot of $J^{(\ell,s)}$ vs. α, we find a family of curves, one for each value of C, which approach a common limiting curve characteristic of the attractive part of the potential alone, as shown in Fig. 1 for $J^{(1,1)}$ with $C = 10$, and $C = 20$.

The uncertainty in the numerical intergrations is estimated to be no worse than 1 or 2 parts in 1000. Values of $J^{(1,1)}$ and $J^{(2,2)}$ were read off large-scale graphs at round values of α, and are given in Table I. This process did not appreciably increase the numerical

uncertainty. The collision integral ratios A*, B*, and C*, which occur in gas mixture formulas,[7] are also given in Table I. The ratio A* was calculated directly from the definition, but B* and C* were calculated from the identities

$$C^* = 1 - \frac{2}{3\alpha} - \frac{1}{3} \frac{d\ln J^{(1,1)}}{d\alpha} , \tag{5}$$

$$B^* = C^*(4-3C^*) + \frac{dC^*}{d\alpha} . \tag{6}$$

The ratio E* which occurs in some of the higher approximations, was also calculated from an identity,

$$E^* \equiv \Omega^{(2,3)*} / \Omega^{(2,2)*} = 1 - \frac{1}{2\alpha} - \frac{1}{4} \frac{d\ln J^{(2,2)}}{d\alpha} . \tag{7}$$

The derivatives, which contribute less than one percent to the results, were evaluated by numerical differentiation. Because of the smallness of the derivatives, the ratios B*, C*, and E* can be given to one more significant figure than the other quantities in Table I.

III. DISCUSSION

A remarkable result noticed in the present calculations is that T* must be very low indeed before the effect of the repulsive core has disappeared, of the order of 10^{-2} or 10^{-3}. In view of this result, we have not extended the tabulations to low values of α, which would correspond to larger values of T*. For such cases, the full results for the Morse potential[6] should probably be used.

The results for the repulsive exponential and for Brokaw's estimates of the present values of $J^{(1,1)}$ and $J^{(2,2)}$ are shown in Fig. 1 for comparison with the present calculations. All three results are in reasonable accord for $J^{(2,2)}$, but for $J^{(1,1)}$ Brokaw's estimates are quite

far off and the repulsive exponential values are reasonably close. This is surprising, and in fact is just the reverse of what we had expected. We conjecture that this is due to the different conditions at the potential origin for an exponential potential and for the inverse power potentials upon which Brokaw based his estimates. The exponential is finite at the origin, whereas the inverse power is singular. It is already known from the results for inverse power potentials that the $\ell = 1$ integrals are sensitive to the conditions at the origin , but that the $\ell = 2$ integrals are independent of them.[3]

In Brokaw's scheme, the attractive exponential is matched in value and slope by an inverse power potential, at a specified mean value of separation distance which varies with temperature. Since this scheme turned out to be poor for $J^{(1,1)}$, it is worthwhile to consider other possibilities for correlating the collision integrals for exponential and inverse power potentials into a single family group. In this connection the correlation scheme used by Baroody[8] for repulsive potentials is of interest. Baroody analyzed the scattering in terms of two energy-dependent parameters, the distance of closest approach in a head-on collision, r_c, and the slope of the potential at this distance, $\gamma = -(d \ln \varphi / d \ln r)_{r_c}$. These choices obviously are inappropriate for an attractive potential, which has $r_c = 0$, but the obvious analogue is the critical distance of closest approach for orbiting, r_o. This is a unique point for an attractive potential. Since orbiting tends to produce isotropic scattering, which is also characteristic of rigid spheres, it might be expected that πr_o^2 would be a good measure of the cross sections.

Such an estimate for the diffusion cross section of ions in neutral gases has been used by Dalgarno, McDowell, and Williams,[9] who call it a "capture" cross section. The slope parameter would then be $\gamma_o = (d \ln \varphi / d \ln r)_{r_o}$. This correlation scheme can be carried through without difficulty, but the results are very similar to Brokaw's. In particular, the predicted $J^{(2,2)}$ is not bad, but the predicted $J^{(1,1)}$ is too high and has the wrong temperature dependence.

We conclude that collision integrals for attractive exponential potentials are not necessarily similar to collision integrals for attractive inverse power potentials, although there does seem to be a close similarity for repulsive potentials, as shown by Brokaw.

In view of the foregoing results, it is worthwhile to investigate the errors to be encountered in calculations of high-temperature gas transport properties when the "tails" of potential energy curves are represented by attractive exponentials. A simple procedure is to assume some potential model to be the exact potential, curve-fit the "tail" of the model curve by an exponential, and see how much error in the collision integrals results. We have selected the Morse potential to represent an exact interatomic potential.[10] For C = 20, we find graphically that the Morse potential can be well represented for $\varphi(r) = 0.5\epsilon$ to 0.01ϵ by the expression

$$\varphi(r) = -(1.7\text{x}10^{14}\epsilon)\exp(-r/0.033\ ). \tag{7}$$

The quantities which directly determine the transport coefficients are the products $\sigma^2\Omega^{(\ell,s)*} = \alpha^2\rho^2 J^{(\ell,s)}$. We should therefore compare the Morse values of $\Omega^{(\ell,s)*}$ with $(0.033\alpha)^2 J^{(\ell,s)}$, where $\alpha = \ln(1.7\text{x}10^{14}\epsilon/kT)$. Such a comparison is shown in Table II for several values of kT/ϵ. All the

TABLE I

Collision integrals for the exponential attractive potential

α	$J^{(1,1)}$	$J^{(2,2)}$	A*	B*	C*	E*
18	0.903	1.006	1.114	1.0751	0.9615	0.9723
20	0.910	1.005	1.104	1.0669	0.9656	0.9751
22	0.916	1.004	1.096	1.0611	0.9686	0.9774
24	0.922	1.004	1.089	1.0565	0.9711	0.9793
26	0.928	1.003	1.082	1.0522	0.9734	0.9809
28	0.933	1.003	1.076	1.0483	0.9754	0.9821
30	0.937	1.003	1.071	1.0450	0.9771	0.9833
32	0.941	1.003	1.066	1.0421	0.9786	0.9844
34	0.944	1.002	1.061	1.0396	0.9799	0.9853
36	0.947	1.002	1.058	1.0374	0.9810	0.9861
38	0.950	1.002	1.055	1.0355	0.9820	0.9868
40	0.953	1.002	1.052	1.0338	0.9829	0.9875
42	0.955	1.002	1.049	1.0320	0.9838	0.9881
44	0.957	1.002	1.047	1.0306	0.9845	0.9886
46	0.959	1.002	1.045	1.0292	0.9852	0.9891
48	0.961	1.002	1.043	1.0281	0.9858	0.9896
50	0.9625	1.002	1.041	1.0269	0.9864	0.9900
52	0.964	1.001	1.039	1.0260	0.9869	0.9904
54	0.9655	1.001	1.037	1.0247	0.9875	0.9908
56	0.9665	1.001	1.036	1.0237	0.9880	0.9911

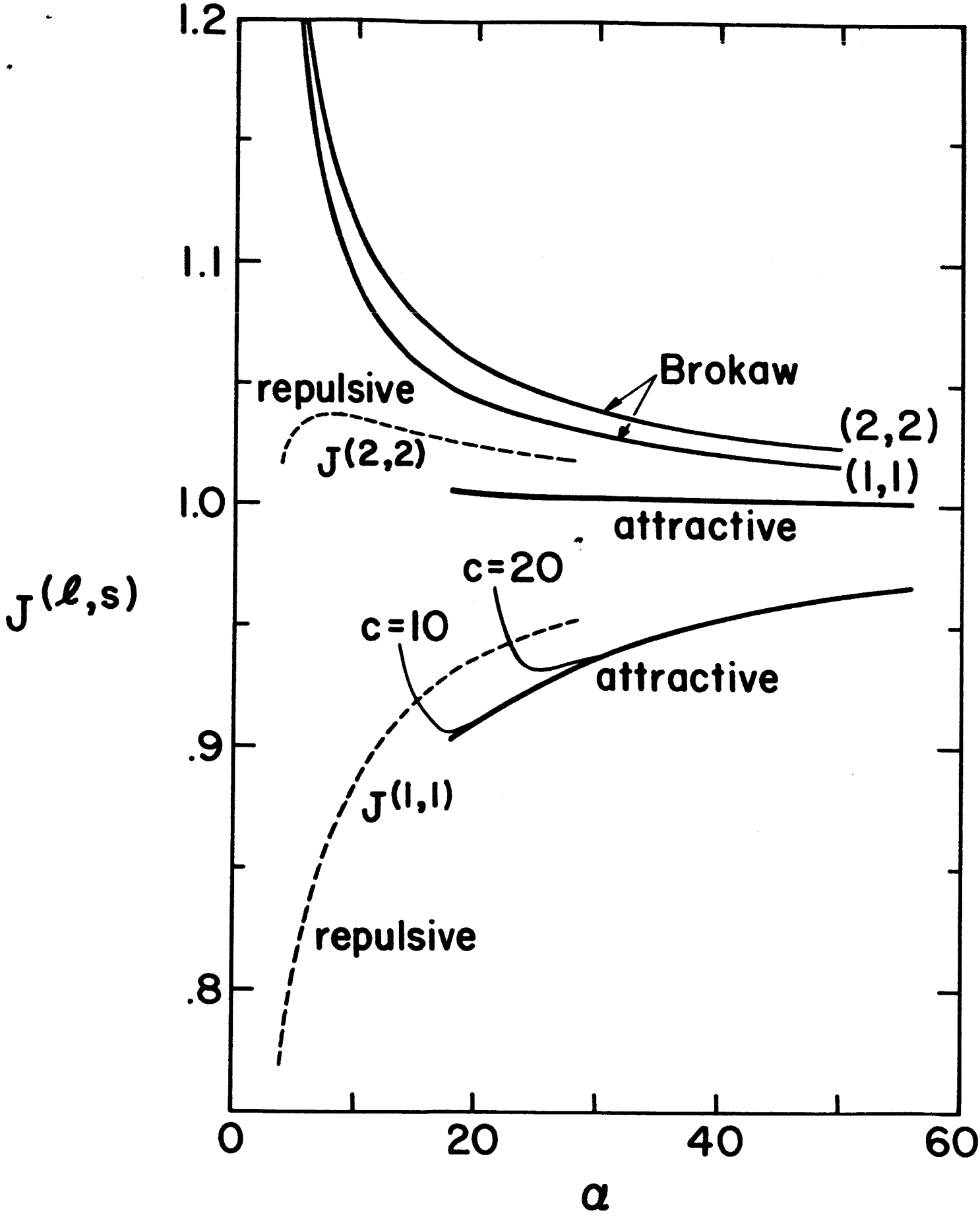
TABLE II

Comparison of collision integrals calculated exactly for the Morse potential with C = 20, and for approximations in which the potential "tail" is fitted by an exponential.

$\frac{kT}{\epsilon}$	$\Omega^{(1,1)*}$			$\Omega^{(2,2)*}$		
	Exact	Present	Brokaw	Exact	Present	Brokaw
0.01	1.5739	1.443	1.556	1.6986	1.524	1.569
0.04	1.4109	1.336	1.443	1.5246	1.413	1.457
0.10	1.3117	1.267	1.372	1.4171	1.342	1.385
0.40	1.1800	1.165	1.266	1.2692	1.238	1.279

FIGURE CAPTION

Fig. 1. Collision integrals for exponential potentials. Solid curves are for an attractive potential, and dashed curves for a repulsive potential. The branches marked C = 10 and C = 20 show how the collision integrals for Morse potentials approach those for the attractive exponential at low temperatures. Brokaw's curves are estimates based on an analogy with inverse power potentials.


1.2
1.1
1.0
.9
.8
0
20
40
60
α
J(ℓ,s)
Brokaw
(2,2)
(1,1)
repulsive
J(2,2)
attractive
c=20
c=10
attractive
J(1,1)
repulsive

REFERENCES

1 J. O. Hirschfelder and M. A. Eliason, Ann. N. Y. Acad. Sci. 67, 451 (1957).

2 J. T. Vanderslice, S. Weissman, E. A. Mason, and R. J. Fallon, Phys. Fluids 5, 155 (1962); K. S. Yun and E. A. Mason, Phys. Fluids 5, 380 (1962); P.H. Krupenie, E. A. Mason, and T. J. Vanderslice, J. Chem. Phys. 39, 2399 (1963).

3 T. Kihara, M. H. Taylor, and J. O. Hirschfelder, Phys. Fluids 3, 715 (1960).

4 L. Monchick, Phys. Fluids 2, 695 (1959).

5 R. S. Brokaw, Phys. Fluids 4, 944 (1961).

6 F. J. Smith and R. J. Munn, J. Chem. Phys. 41, 0000 (1964).

7 J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, Molecular Theory of Gases and Liquids (John Wiley and Sons, Inc., New York, 1954). Chap. 8.

8 E. M. Baroody, Phys. Fluids 4, 1182 (1961); Phys. Rev. 124, 745 (1961); Phys. Fluids 5, 925 (1962).

9 A. Dalgarno, M. R. C. McDowell, and A. Williams, Phil. Trans. Roy. Soc. (London) A250, 411 (1958).

10 This procedure was suggested to us by Dr. W. L. Bade.