Enskog and van der Waals play hockey

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We consider the mean free path of a hockey puck in a system of other pucks on an air table, and show how the simple low-density kinetic-theory value for this mean free path can be extended to higher densities. This approach is connected both with the Enskog theory of the transport properties of dense gases and with the van der Waals theory of the equation of state of dense gases. We derive several simple approximations for the high-density mean free path, and compare the results with each other, with accurate computer-simulation results, and with experimental results obtained in the freshman physics laboratory of the University of Maryland. We present the arguments in both simplified and more elaborate forms.

I. INTRODUCTION

Among the many experiments that can be performed on air table is one in which the mean free path between collisions of a marked puck is measured.[1] If the density of pucks is high enough that collisions of the marked puck with the walls do not predominate, it is usually found that the measured mean free path is appreciably smaller than that calculated from the classical kinetic-theory formula,[2]

$$\lambda_{12}^{-1} = [1 + (m_1/m_2)]^{1/2} n_2 Q_{12}, \tag{1}$$

where λ_{12} is the mean free path of the marked puck 1 of mass m_1 moving in a collection of pucks of mass m_2 having "density" n_2 (pucks per unit area), and Q_{12} is the collision cross section, which in two dimensions is

$$Q_{12} = \sigma_1 + \sigma_2, \tag{2}$$

where σ_1 and σ_2 are the puck diameters. The mass factor on the right of Eq. (1) accounts for the average relative velocity of collisions. Note that Eq. (1) also holds in three dimensions for rigid spheres, with n_2 equal to the number of spheres per unit volume, but Eq. (2) must be replaced in three dimensions by $Q_{12} = (\pi/4)(\sigma_1 + \sigma_2)^2$. After analyzing various sources of experimental error, one usually concludes that this reduction of the mean free path is a genuine effect related to the fact that the density of the system is too large for Eq. (1) to hold very accurately.

The purpose of this paper is to show how this density effect can be accounted for in a simple way in terms of an excluded "volume" (really area). This provides a simple introduction to theories of dense gases, since the same effect plays a central role in both the van der Waals theory of the equation of state[3,4] and the Enskog kinetic theory of transport properties.[5-7] That is, we will obtain a correction factor χ_{12} for the mean free path,

$$\lambda_{12} = \lambda_{12}^0/\chi_{12}, \tag{3}$$

where λ_{12}^0 is the low-density value given by Eq. (1). The same correction factor occurs in the Enskog expressions for such properties as the diffusion coefficient D_{12},

$$D_{12} = D_{12}^0/\chi_{12}, \tag{4}$$

where D_{12}^0 is the low-density kinetic-theory result. In the case that the mass and diameter of the tagged particle are the same as those of the rest of the particles, the same correction factor χ occurs in the equation of state for the pressure P,

$$P = nkT(1 + nb\chi), \tag{5}$$

where k is Boltzmann's constant, T is the temperature, and b is the van der Waals covolume. The covolume is equal to one-half the total volume excluded by the finite molecular size, which in two dimensions is

$$b = (\pi/2)\sigma^2, \tag{6}$$

and in three dimensions is $b = (2\pi/3)\sigma^3$. The physical interpretation of χ is that it is the radial distribution function for pairs of particles, evaluated just outside the point of contact.

In what follows we show first how the mean free path should be corrected in terms of Enskog's χ, but do not attempt to calculate χ in terms of the properties of the system. We then show how the same quantity enters into the equation of state. This enables us to make a simple approximate calculation of χ using the van der Waals equation of state. We next show how an improved expression for χ can be obtained by combining a medium-density correction to the van der Waals formula (which counts the overlapping of three or more disks or spheres incorrectly) with the high-density cutoff imposed by close packing. The improvement is straightforwardly achieved by a Padé approximant, which serves to introduce another technique of current interest in physics[8,9] in a very simple setting. Comparison is made with essentially exact computer-simulation results, and with experimental results obtained in the freshman physics laboratory at the University of Maryland.

All these results can be obtained, or at least made plausible, through rather simplified arguments suitable for undergraduates. As a final embellishment, we show in an Appendix how the arguments can be made more rigorous and mathematical where necessary. We give these results for a binary mixture of two kinds of particles, in order to formulate the theory in a context where it can apply to a wide variety of air table experiments.

II. THE MEAN FREE PATH AND THE RADIAL DISTRIBUTION FUNCTION χ

According to the elementary kinetic theory of gases, the mean free path of a gas molecule is equal to the product of the average time between collisions and the average speed of a molecule. For a gas in equilibrium the average speed of a molecule does not depend on the density of the gas, but the average time between collisions does. This quantity is the inverse of the collision frequency, and to account for the density dependence of the mean free path we must determine the density dependence of this collision frequency. It is almost intuitively obvious that the collision frequency is directly proportional to the number density in the immediate neighborhood of a molecule we focus our attention on. In a dilute gas this number density is uniform throughout the gas, but in a dense gas the density near a particular molecule is greater than the average. This increase can be attributed to a shielding effect which produces an effective attraction between the two particles. This "attraction" is due to the fact that the parts of molecules 1 and 2 which are closest to each other are shielded from collisions with other particles in the gas, as illustrated in Fig. 1. Hence, the other molecules in the gas have a tendency to force two molecules closer together once they get sufficiently close. If we measure the excess number density of molecules of species 2 next to a molecule of species 1 by χ_{12}, defined as

$$\chi_{12} = n_2(\sigma_{12})/\bar{n}_2, \tag{7}$$

where $n_2(\sigma_{12})$ is the density just outside the contact surface between 1 and 2 and $\bar{n}_2$ is the average number density throughout the whole gas, then the collision frequency ν_{12} for a molecule of species 1 with molecules of species 2 is

$$\nu_{12} = \chi_{12}\nu_{12}^0, \tag{8}$$

where ν_{12}^0 is the collision frequency that would occur in the absence of the shielding "attraction." From this the mean free path follows as $\lambda_{12} = \lambda_{12}^0/\chi_{12}$, as already given in Eq. (3), provided that species 1 is present only in trace amounts, so that 1–1 collisions have a negligible effect on the free path.

An interesting historical sidelight is that an attraction caused by a shielding from collisions was long ago proposed as a mechanism to explain gravitational attraction.[10] An all-pervasive isotropic wind of particles was supposed to exist throughout space, and the mutual shielding of two bodies near each other produced an effective attraction. This explanation of gravitational attraction accounts for the inverse-square law of force, but fails on other counts.[10] It is amusing to find this supposedly long-dead mechanism alive and well in the theory of dense gases, although it does not lead to an inverse-square law in gases because the "wind" particles are not undeflected.

It is clear that the calculation of Enskog's χ in terms of densities and molecular diameters is no easy task, since it is basically a many-body problem. It represents a "collective" effect of the gas as a whole. Indeed, no closed analytical expression for χ is known, and our central task will be to obtain simple but useful approximations for χ. Before tackling this problem, however, let us first sharpen up the argument for taking the collision frequency proportional to the number density. Consider how one would compute the number of collisions that take place in a small time interval δt between molecules of species 1 in a mixture with
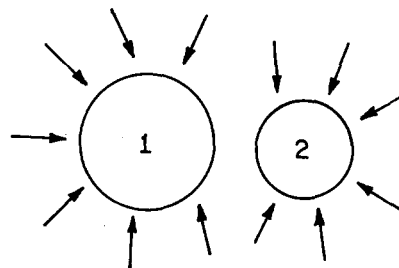

Fig. 1. The shielding of the adjacent parts of particles 1 and 2 from other particles in the gas, for small separation of the particles, produces an effective attraction between the two particles.

those of species 2. To find the number of collisions that take place in time δt between molecules of species 1 with velocity $\mathbf{v}_1$ and molecules of species 2 with velocity $\mathbf{v}_2$, we construct a collision cylinder of volume $Q_{12}|\mathbf{v}_1 - \mathbf{v}_2|\delta t$ centered on each molecule of species 1 with velocity $\mathbf{v}_1$, and ask how many molecules of species 2 with velocity $\mathbf{v}_2$ are inside these collision cylinders at the start of the small time interval. For a dilute gas, one makes the assumption that the number of such molecules of species 2 can be computed as if they were distributed at random in the collision cylinders with the same uniform density as they are in the container as a whole. Then the collision frequency is found by integrating over all velocities $\mathbf{v}_1$ and $\mathbf{v}_2$ and dividing by the time interval δt. The average collision frequency for one molecule of species 1 with molecules of species 2, that is ν_{12}^0, is then obtained by dividing the result by N_1, the number of species 1 molecules. The result is that ν_{12}^0 is directly proportional to $\bar{n}_2$.

At high enough densities, the assumption that the distribution of molecules of species 2 in the collision cylinders is the same as that in the gas as a whole breaks down. In fact, if the volume occupied by the molecules themselves is an appreciable fraction of the total volume of the system, then the probability of finding a particle in a collision cylinder is greater than that for finding a particle in an equal volume placed at random in the gas, because of the "attractive" effect discussed above. However, we need to know this increased probability only at the point of contact of the two particles. It is easy to see that this special point is singled out when we let $\delta t \rightarrow 0$ in the calculation of the collision frequency, since in this limit the collision cylinders shrink to a small region about the point of contact. From these arguments we conclude that the collision frequency at higher densities is proportional to $\chi_{12}\bar{n}_2$, or $\nu_{12} = \chi_{12}\nu_{12}^0$ as already given in Eq. (8).

III. THE EQUATION OF STATE AND χ

In this section we will explain how the factor χ discussed in the previous section is related to the pressure. We will consider only a single-component system here, and reserve the treatment of mixtures for the Appendix.

The pressure is calculated as the net rate of flow of the component of momentum in the positive x direction across a reference plane (reference line in two dimensions) perpendicular to x. There are two mechanisms that contribute to the momentum flux. The first is the translational transfer where a particle carries its own momentum across the reference plane (line). The second is the collisional transfer of momentum, where a particle with its center on one side of the plane collides with another particle whose center is
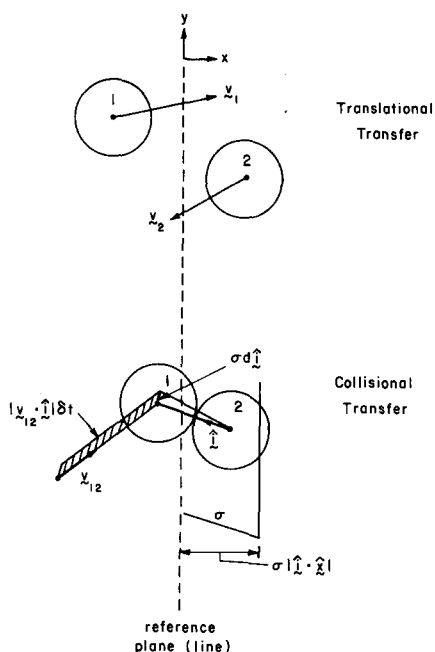
Fig. 2. Transfer of momentum across a reference plane (or line in two dimensions) represented by the dashed line. The two upper particles transfer momentum by the translational mechanism of crossing the reference plane (line). The two lower particles transfer momentum from particle 1 to particle 2 by collision, without the center of either particle crossing the reference plane (line). The geometrical constructions shown around the lower two particles are used in the calculation of the collisional transfer of momentum given in the Appendix.

on the other side of the plane, and there is an instantaneous transfer of momentum from the center of one particle to the center of the other particle. These two mechanisms are illustrated in Fig. 2.

The contribution to the pressure from the translational mechanism is a calculation familiar in elementary kinetic theory.[2] Briefly, particles moving from left to right in Fig. 2 carry momentum $+mv_x$ per particle, and there are $\frac{1}{2}nv_x$ crossing unit area in unit time. These particles thus contribute $\frac{1}{2}nmv_x^2$ to the pressure. Particles moving from right to left carry momentum $m(-v_x)$ and there are $\frac{1}{2}n(-v_x)$ crossing, so that these also contribute $\frac{1}{2}nmv_x^2$ to the pressure. Combining these two translational contributions, and averaging over any distribution of velocities, we obtain

$$P_{trans} = nm\langle v_x^2\rangle, \qquad (9)$$

where the angular brackets signify the average over the velocity distribution. The components of the velocity are related to the total velocity by the Pythagorean theorem, so that we obtain for any number of dimensions the result

$$\langle v_x^2\rangle = (1/d)\langle v^2\rangle, \qquad (10)$$

where d is the dimensionality of the space. The translational contribution to the pressure is thus

$$P_{trans} = (1/d)nm \langle v^2\rangle = nkT, \qquad (11)$$

where the last equality follows from the identification of temperature in an ideal gas in which there is no collisional transfer.

The calculation of the collisional transfer contribution is similar to the calculation of the collision frequency in Sec. II. The geometrical details of the calculation get somewhat

complicated and are deferred to the Appendix, but the gist of the argument is quite straightforward. First, the collisional transfer of momentum will be proportional to the momentum carried up to the reference plane by particles 1 (Fig. 2). We thus expect P_{coll} to contain a factor of $nm\langle v_x^2\rangle$ or nkT, just as does P_{trans}. Second, the collisional transfer must be proportional to the number of particles on the other side of the reference plane that collide with particles 1, so that the transfer of momentum can take place. This number is in turn proportional to the number density of particles 2 times a volume of the order of a molecular size. P_{coll} thus contains a factor proportional to nb in addition to the factor of nkT, where b is the covolume. We assume that the coefficient of proportionality is unity. Finally, if the gas is dense, there is an enhancement of the density of particles 2 nearby to particles 1, because of the "attraction" discussed previously and shown in Fig. 1. This gives a further factor of χ. The final result is

$$P_{coll} = (nkT)(nb\chi). \qquad (12)$$

The appearance of the covolume b is not especially surprising—it has to appear for dimensional reasons if nothing else—but it is a bit surprising that the exact calculation as given in the Appendix shows that the numerical factor in Eq. (12) is unity in both two and three dimensions (as well as in one dimension). The total pressure of the gas at any density is therefore

$$P = P_{trans} + P_{coll} = nkT(1 + nb\chi). \qquad (13)$$

This seemingly solves the famous problem of the equation of state of a dense gas of rigid spheres (disks), but of course we have not solved the problem at all, we have only pushed it over into the problem of finding χ. In fact, we will use Eq. (13) in reverse, so to speak, and obtain an approximate expression for χ from the van der Waals equation of state.

IV. THE VAN DER WAALS ESTIMATE OF χ

The van der Waals equation of state attributes deviations from ideality to two causes—the finite size of the molecules, and attractive forces between molecules. The finite size increases the pressure by reducing the effective volume of the container from V to $V - Nb$, where N is the number of molecules in V, and b is the familiar covolume. The attractive forces decrease the pressure by retarding the impacts of molecules on the container walls. The result can be written as

$$P = NkT/(V - Nb) - a(N/V)^2. \qquad (14)$$

For a gas whose particles interact only with hard-core repulsions, a can be set equal to zero, and the van der Waals equation can be written as

$$P = nkT/(1 - nb), \qquad (15)$$

where $n = N/V$. If we combine this with the exact equation of state derived in the previous section, Eq. (13), we obtain

$$1 + nb\chi_{vdW} = 1/(1 - nb) \qquad (16)$$

or

$$\chi_{vdW} = 1/(1 - nb). \qquad (17)$$

The accuracy of this approximation can be tested for a gas

Table I. Comparison of exact (computer-simulated) and approximate values of χ as a function of density for a gas of rigid disks.

$n\sigma^2$	$\dfrac{n\sigma^2}{(n\sigma^2)_{cp}}$	Exact χ Refs. 11–13	χ_{vdW} Eq. (17)	χ_{vdW}^{mod} Eq. (23)	Padé χ	
					cp, Eq. (24)	rp, Eq. (26)
0	0	1.000	1.00	1.000	1.000	1.000
0.115	0.1	1.159	1.22	1.165	1.158	1.160
0.231	0.2	1.378	1.57	1.396	1.355	1.366
0.385	0.333	1.786	2.53	1.897	1.709	1.756
0.462	0.4	2.058	3.64	2.311	1.946	2.031
0.577	0.5	2.683	10.74	3.439	2.418	2.620
0.691	0.6	3.637		6.713	3.128	3.615
0.850	0.736	6.22			4.96	7.05

of hard disks by comparing values obtained in this way with very precise values obtained from computer calculations of the equation of state.[11–13] This comparison is given in Table I and Fig. 3, which also show other approximate results to be discussed in subsequent sections.

One can see that the approximation of Eq. (17) is not too bad at low densities, but is very poor at densities greater than that corresponding to about one-third the density of close packing of the disks, which is

$$(n\sigma^2)_{cp} = 2/\sqrt{3} = 1.15. \qquad (18)$$

Here the subscript cp stands for "close packed." The close-packed density is the density of the collection of disks when they are compressed into as small an area as possible, taking into account the fact that they cannot penetrate each other. In the close-packed state the disks form a crystalline array whose density is given by Eq. (18). As the density of the disks approaches the close-packed density, the pressure exerted by the disks on the walls increases because of the mutual repulsions of the disks. At the close-packed density the pressure becomes infinite because the disks cannot be compressed any further. Thus we expect that as $n\sigma^2$ approaches $(n\sigma^2)_{cp}$, then χ^{-1} approaches zero according to Eq. (13). Study of Fig. 3, a plot of χ^{-1} vs $n\sigma^2$, shows that the van der Waals approximation fails in two major respects. First, χ_{vdW}^{-1} goes to zero at $nb = 1$ or at $n\sigma^2 = 2/\pi = 0.64$, instead of near the close-packed density of 1.15. Second, the initial slope of χ_{vdW}^{-1} vs $n\sigma^2$ is incorrect. Both of these failures are easily corrected by simple calculations, which can be used to obtain a much improved approximation for χ, as discussed in Sec. V.

V. IMPROVED APPROXIMATIONS FOR χ

We consider first the correction for the initial slope in Fig. 3. The trouble can be traced to the correction for excluded

volume in the van der Waals theory. The idea of an excluded volume is sound, but the calculation of it as Nb is correct only when just pairs of particles are considered, and involves errors when three or more particles are considered simultaneously. The nature of the difficulty is shown in Fig. 4, where the region forbidden to a test particle by two other particles is shown. If the two particles are well separated, the total forbidden region is $2\pi\sigma^2$ (in two dimensions), but if they are close together the total is smaller because the overlapping portion of the forbidden regions should be counted only once, not twice. To make this idea more precise, we expand the pressure of the gas as a power series in the density (the well-known virial expansion),

$$P = nkT(1 + nB_2 + n^2B_3 + n^3B_4 + \cdots), \qquad (19)$$

where B_2, B_3, etc., are called second, third, etc., virial coefficients. By comparison of Eqs. (13) and (19), we see that the corresponding virial expansion for χ is

$$\chi = (B_2/b) + n(B_3/b) + n^2(B_4/b) + \cdots. \qquad (20)$$

The van der Waals expression, obtained by expansion of Eq. (15), is

$$P = nkT(1 + nb + n^2b^2 + n^3b^3 + \cdots). \qquad (21)$$

The excluded volume due to just pairs has been counted correctly in the van der Waals expression, so that $B_2 = b$, but the values of B_3 and higher virial coefficients are incorrect because of the overlap problem illustrated in Fig. 4. However, we need correct only B_3, which deals with just triplets of particles, to get the correct value of the initial slope of χ^{-1} in Fig. 3. The third virial coefficient B_3 can be computed analytically by the procedure outlined in the
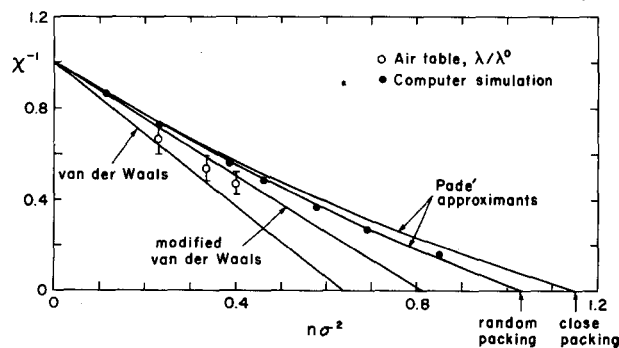

Fig. 3. Comparison of exact (computer-simulated) and approximate values of χ^{-1} as a function of reduced density $n\sigma^2$ for a gas of rigid disks of diameter σ.
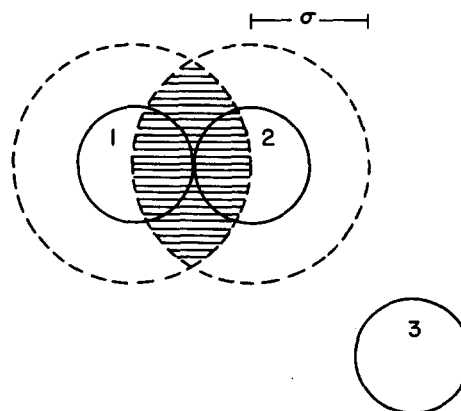

Fig. 4. Regions forbidden to particle 3 by particles 1 and 2 are shown by the dashed circles. In the van der Waals theory, the lens-shaped hatched region is erroneously counted twice. The area of this region is $\sigma^2[(2\pi/3) - (\sqrt{3}/2)]$.

Appendix, and involves the computation of the shaded area indicated in Fig. 4. For a two-dimensional gas of rigid disks, B_3 is given by

$$B_3 = [(4/3) - (\sqrt{3}/\pi)]b^2. \tag{22}$$

Thus it seems that a better approximation to χ, which has a form similar to the approximate Eq. (17) but which correctly predicts the initial slope, is given by

$$\chi_{vdW}^{mod} = \{1 - nb[(4/3) - (\sqrt{3}/\pi)]\}^{-1}. \tag{23}$$

This will give the correct initial slope in Fig. 3. Its accuracy is compared with exact results in Table I and Fig. 3. Although a considerable improvement over the simple van der Waals result is achieved, Eq. (23) is still poor at high densities, presumably because χ^{-1} goes to zero at $n\sigma^2 = 0.81$, instead of near the close-packed density.

This last observation suggests that better results could be achieved if we could write an approximation for χ that behaved like Eq. (23) at low densities, but that went to infinity (χ^{-1} going to zero) at the close-packed density. Such a combination of behavior is readily achieved through the mathematical device of Padé approximants, which have found many applications in physics.[8,9] A Padé approximant as we will use it here is simply a ratio of polynomials whose coefficients are chosen so that the zeroes of the polynomial in the numerator reproduce the known zeroes of the function being approximated, and the zeroes of the polynomial in the denominator reproduce the known infinities of the function. Additional coefficients can be chosen to correctly reproduce a few terms of known series expansions, such as the virial expansion. In the present case, our Padé approximant will be a ratio of two expressions linear in n, the two adjustable coefficients being chosen to reproduce the infinity in χ. If we take the close-packed density corresponding to a completely regular crystalline packing of disks as given by Eq. (18), the Padé approximant is

$$\chi_{Padé}^{cp} = \left[1 + \frac{n\sigma^2}{(n\sigma^2)_{cp}} \left(\frac{4\pi}{3\sqrt{3}} - 2 \right) \right] \bigg/ \left[1 - \frac{n\sigma^2}{(n\sigma^2)_{cp}} \right], \tag{24}$$

with $(n\sigma^2)_{cp} = 2/\sqrt{3}$. This expression is compared with the other approximations and with the precise computer results in Table I and Fig. 3. The agreement is quite good, but can be improved even further by one simple observation.

The observation is that continued compression of a gas of rigid disks is likely to produce "jamming" (i.e., infinite P and infinite χ) when the disks are still arranged randomly, since they probably will be unable to adjust themselves into a perfect crystalline order. Some simple experiments with lucite disks have shown that the density of such random packing is about 11% less than regular close packing,[14] so that

$$(n\sigma^2)_{rp} = 0.89(n\sigma^2)_{cp}, \tag{25}$$

where the subscript rp stands for "randomly packed." The corresponding Padé approximant for χ is then

$$\chi_{Padé}^{rp} = \left(1 + \frac{n\sigma^2}{(n\sigma^2)_{cp}} \left\{ \frac{4\pi}{3\sqrt{3}} - \left[1 + \frac{(n\sigma^2)_{cp}}{(n\sigma^2)_{rp}} \right] \right\} \right) \bigg/ \left[1 - \frac{n\sigma^2}{(n\sigma^2)_{rp}} \right]. \tag{26}$$

The agreement of this expression with the computer results

is quite good, as shown in Table I and Fig. 3.

As a final comment, the foregoing approximations for χ in two dimensions are easily extended to any number of dimensions by writing them in terms of the corresponding covolume b and third virial coefficient B_3, as follows:

$$\chi_{vdW} = (1 - nb)^{-1}, \tag{27}$$

$$\chi_{vdW}^{mod} = [1 - n(B_3/b)]^{-1}, \tag{28}$$

$$\chi_{Padé}^{cp} = \left\{ 1 + nb \left[\frac{B_3}{b^2} - \frac{1}{(nb)_{cp}} \right] \right\} \bigg/ \left[1 - \frac{nb}{(nb)_{cp}} \right]. \tag{29}$$

The expression for $\chi_{Padé}^{rp}$ is obtained from Eq. (29) by replacing $(nb)_{cp}$ by $(nb)_{rp}$. For reference, the three-dimensional values of the quantities in Eqs. (27)–(29) are

$$b = (2\pi/3)\sigma^3, \tag{30a}$$

$$B_3 = (5/8)b^2 \quad \text{(Ref. 6)}, \tag{30b}$$

$$(n\sigma^3)_{cp} = \sqrt{2} \quad \text{(Ref. 15)}, \tag{30c}$$

$$(n\sigma^3)_{rp} = 0.869(n\sigma^3)_{cp} \quad \text{(Ref. 16)}. \tag{30d}$$

IV. APPLICATION TO AIR TABLE EXPERIMENTS

A number of experiments were carried out in the laboratory by placing pucks on an air table with a motor-driven device at the boundaries designed to keep the pucks in constant motion. One of the pucks had a light at its center and its motion was photographed to record its trajectory over a certain time interval.[1] The system should have been isothermal, but because of friction on the table and inelastic collisions between pucks, the system was "colder" and denser at the center of the table than at the outer edges. A polaroid camera was mounted above the table and its field of view was restricted to the central part of the table where the temperature and density appeared to be roughly uniform.

From an enlargement of the polaroid photograph, the number of free paths longer than or equal to x, $N(x)$, was determined as a function of x. The mean free path λ was determined by assuming that $N(x)$ had the form

$$N(x) = N_0 e^{-x/\lambda}, \tag{31}$$

which is a good approximation following from kinetic theory.[1] The value of λ was then found as a best-fit slope of a semilogarithmic plot of the data. This procedure gives more reliable values of λ than the direct procedure of calculating $\bar{x}$ and taking $\bar{x} = \lambda$, because of the difficulty of recognizing very glancing collisions on the photograph, and of properly counting very long and very short free paths.

The results of three experimental values for λ/λ^0 at different densities are given in Fig. 3, where λ^0 is the theoretical low-density value given by Eq. (1). These experimental values can be directly compared with the values of χ^{-1} shown in Fig. 3 and discussed previously. The experimental values are in reasonably good agreement with the precise computer-simulated values, and any of the various approximations to χ would be adequate for describing the experimental results within their likely uncertainty. We estimate that the uncertainty in the air-table values to be about ± 10%–15%, and have shown error bars of ±10% in Fig. 3. There are a number of sources of error in these experiments. The system may not be in equilibrium, the

density of pucks in the photographed area is neither uniform nor constant over an experimental run, and it is difficult to properly count the free paths on the photographs, especially the longest and shortest ones. Effects due to the finite size of the air table and the finite number of pucks may be of some importance. Notice that a correction for the higher density at the center of the table would shift the experimental points into closer agreement with the computer results.

The experiments described above were carried out to test the theoretical predictions given in the earlier sections of this paper. They were somewhat more carefully done than a typical experiment carried out in the freshman laboratory. Therefore we now present one of the typical experimental runs carried out by the freshmen. The usual experiment consists in measuring the mean free path of one large puck with a light on it, in a system composed of a number of smaller pucks, all of which have the same diameter. The density of the small pucks was calculated by dividing the total number of small pucks by the total area available to the center of each of the pucks; this procedure thus includes a small correction for the layer of excluded area next to the boundaries. The large puck had a diameter of 6.8 cm, and the small pucks had diameters of 3.6 cm. At a density of small pucks of 0.014 pucks/cm^2, the measured value of λ/λ^0 was 0.68. Using the modified van der Waals expression for χ, as generalized for a mixture in the Appendix, we calculate a theoretical value for λ/λ^0 of 0.76, which agrees with the experimental value to within 11%, which seems satisfactory.

In conclusion, we have presented here some simple theoretical methods for computing the mean free paths of pucks on an air table at high densities, which can be successfully used to treat typical laboratory experiments on the mean free path.

ACKNOWLEDGMENT

APPENDIX: MORE RIGOROUS DERIVATIONS FOR MIXTURES

Here we make the arguments of the text more rigorous, and include the extension to mixtures. There are three calculations to be considered—the collision frequency, the collisional-transfer contribution to the pressure, and the virial expansions for P and χ.

Collision frequency

We begin, as before, by constructing a collision cylinder of volume $Q_{12}|v_1 - v_2|\delta t$ on each molecule of species 1 with velocity v_1. The number of molecules of species 1 with velocities between v_1 and $v_1 + dv_1$ is given by $n_1\phi(v_1)dv_1$, where $\phi(v_1)$ is the Maxwell–Boltzmann equilibrium distribution function,

$$\phi(v_1) = (\beta m_1/2\pi)^{d/2}\exp(-\beta m_1 v_1^2/2), \quad (A.1)$$

where $\beta = (kT)^{-1}$ and d is the number of dimensions of the system. A similar expression holds for species 2. For a dilute gas, the number of molecules of species 2 with velocity v_2 in the collision cylinders is proportional to the average (uniform) density of such species 2 molecules in the container, which is $n_2\phi(v_2)dv_2$. Integrating over all velocities v_1 and v_2, and dividing by n_1, we obtain the average collision frequency, ν_{12}^0, for a molecule of species 1 with molecules of species 2 as

$$\nu_{12}^0 = n_2 Q_{12} \int dv_1 \int dv_2 |v_1 - v_2| \, \phi(v_1)\phi(v_2). \quad (A.2)$$

In a dense gas the number of molecules of species 2 in the collision cylinders is increased to $n_2\chi_{12}\phi(v_2)dv_2$, so that the collision frequency becomes

$$\nu_{12} = n_2\chi_{12}Q_{12} \int dv_1 \int dv_2 |v_1 - v_2| \, \phi(v_1)\phi(v_2)$$
$$= \chi_{12}\nu_{12}^0. \quad (A.3)$$

Similarly, the frequency of collisions of a molecule of species 1 with other particles of the same species is

$$\nu_{11} = n_1\chi_{11}Q_{11} \int dv_1 \int dv_1' |v_1 - v_1'| \, \phi(v_1)\phi(v_1')$$
$$= \chi_{11}\nu_{11}^0, \quad (A.4)$$

where $\chi_{11} = n_1(\sigma_{11})/\bar{n}_1$ is the radial distribution at contact for two particles of species 1. Of course, both χ_{11} and χ_{12} must be computed by taking into account the fact that the system is a binary mixture.

To compute the mean free path λ_1 for a typical molecule of species 1, we compute the average time between collisions, τ_1, as

$$\tau_1 = (\nu_{12} + \nu_{11})^{-1}, \quad (A.5)$$

and then multiply τ_1 by the average speed of a molecule of species 1, $\bar{v}_1$,

$$\bar{v}_1 = \int_0^\infty v_1\phi(v_1)v_1^{d-1}dv_1 \Big/ \int_0^\infty \phi(v_1)v_1^{d-1}\,dv_1. \quad (A.6)$$

For $d = 2$, $\bar{v}_1 = (\pi kT/2m_1)^{1/2}$, and for $d = 3$, $\bar{v}_1 = (8kT/\pi m_1)^{1/2}$. Therefore the mean free path λ_1 is

$$\lambda_1 = \bar{v}_1(\nu_{12} + \nu_{11})^{-1} = \bar{v}_1(\chi_{12}\nu_{12}^0 + \chi_{11}\nu_{11}^0)^{-1}$$
$$= [\chi_{12}(\lambda_{12}^0)^{-1} + \chi_{11}(\lambda_{11}^0)^{-1}]^{-1}, \quad (A.7)$$

where

$$(\lambda_{ij}^0)^{-1} = [1 + (m_i/m_j)]^{1/2}n_jQ_{ij}. \quad (A.8)$$

Two special cases are of interest here. For a pure one-component system, the mean-free path is given by

$$\lambda_1 = \lambda_1^0/\chi_1, \quad (A.9)$$

where λ_1^0 is the low-density value and χ_1 is the radial distribution at contact for a one-component system. The other case of interest occurs when species 1 is present in only trace amounts. In the particular case of interest here, species 1 consists of a marked puck whose mass and diameter are different from those of the remaining pucks on the air table. The mean free path for the marked puck is then given by

$$\lambda_{12} = \lambda_{12}^0/\chi_{12}, \quad (A.10)$$

where χ_{12} is now the radial-distribution function for finding

a regular puck in contact with the marked one, computed by using the fact that all but the marked puck are mechanically identical.

Collisional-transfer contribution to pressure

Here we wish to derive Eq. (12) for P_{coll} more carefully. We consider only the two-dimensional case for simplicity, and refer to Fig. 2 for notation. Although all the particles are mechanically identical, we denote the particle on the left of the reference line as 1, and the other one as 2. In a 1-2 collision, the vector, $r_{12} = r_1 - r_2$, between the centers of the particles at the instant of collision can be written as

$$r_{12} = \hat{i}\sigma, \qquad (A.11)$$

where $\hat{i}$ is a unit vector along the line of centers at impact, and σ is the particle diameter. The condition that the centers of the particles are on opposite sides of the reference line is satisfied if the center of 2 is inside a strip of width $\sigma|\hat{i}\cdot\hat{x}|$, where $\hat{x}$ is a unit vector in the x direction, and if $\hat{i} \cdot \hat{x} < 0$. If particles 1 and 2 have velocities v_1 and v_2, respectively, then the conditions that must be satisfied if a 1-2 collision is to occur in time δt with the line of centers in a preselected direction $\hat{i}$ are as follows: (i) $v_{12} \cdot \hat{i} < 0$, where $v_{12} = v_1 - v_2$; and (ii) the center of particle 1 is in the shaded region shown in Fig. 2, whose area is

$$(|v_{12} \cdot \hat{i}|\delta t)(\sigma d\hat{i}). \qquad (A.12)$$

The number of collisions taking place in time δt such all these conditions are satisfied simultaneously is

$$n^2\phi(v_1)dv_1\phi(v_2)dv_2 \, \chi(\sigma|\hat{i} \cdot \hat{x}|)(|v_{12} \cdot \hat{i}|\delta t)(\sigma d\hat{i})$$
$$\times\theta(-v_{12} \cdot \hat{i})\theta(-\hat{i}\cdot \hat{x}), \quad (A.13)$$

where to remind the reader of the restrictions mentioned above, we have inserted in Eq. (A.13) $\theta(z)$, the step function,

$$\theta(z) = \begin{cases} 1 \text{ for } z \geq 0 \\ 0 \text{ for } z < 0. \end{cases} \qquad (A.14)$$

Furthermore, if the particles make elastic specular collisions, the momentum transfer in the collision from the center of particle 1 to the center of particle 2 is given by $m(v_{12} \cdot \hat{i})\hat{i}$. Thus the collisional-transfer contribution to the pressure is

$$P_{coll} = n^2\chi\sigma^2 \int dv_1 \int dv_2 \int d\hat{i} \, \theta(-v_{12} \cdot \hat{i})$$
$$\times \theta(-\hat{i} \cdot \hat{x})m(v_{12} \cdot \hat{i})(\hat{i} \cdot \hat{x})$$
$$\times|\hat{i} \cdot \hat{x}| \, |v_{12} \cdot \hat{i}|\phi(v_1)\phi(v_2), \quad (A.15)$$

which integrates to

$$P_{coll} = \tfrac{1}{2}\pi kTn^2\chi\sigma^2 = n^2kTb\chi, \qquad (A.16)$$

where $b = \pi\sigma^2/2$ is the van der Waals covolume in two dimensions. This is Eq. (12) as advertised.

In the case of a k-component mixture, the procedure can be generalized by observing that the pressure can be written as the summation

$$P = \sum_{i=1}^{k} \sum_{j=1}^{k} P_{ij}, \qquad (A.17)$$

where P_{ii} contains the contribution to the pressure from the translational motion of particles of species i, and from the collisional transfer between particles of type i, while P_{ij}

consists exclusively of the collisional transfer from particles of species i (on the left of the reference line) to particles of species j (on the right of the reference line). Therefore Eq. (13) generalizes to

$$P_{ij}/n_ikT = \delta_{ij} + n_ib_{ij}\chi_{ij}, \qquad (A.18)$$

where δ_{ij} is the Kronecker delta, and $b_{ij} = \pi\sigma_{ij}^2/2$ is one-half the excluded volume for a particle of species j due to the presence of species i.

Virial expansions for P and χ

The second and third virial coefficients, B_2 and B_3, appearing in Eq. (19) for P are given by the expressions

$$B_2 = -\tfrac{1}{2} \int dr f(|r|), \qquad (A.19)$$

$$B_3 = -\tfrac{1}{3} \int dr_1 \int dr_2 f(|r_1|)f(|r_2|) f(|r_1 - r_2|). \qquad (A.20)$$

Here $f(|r|)$ is the Mayer f function defined by

$$f(|r|) = e^{-\beta V(|r|)} - 1, \qquad (A.21)$$

where $V(|r|)$ is the potential energy of interaction between two particles separated by a distance $|r|$. For a system of hard disks (or spheres) of diameter σ, $f(|r|)$ is given by

$$f(|r|) = \begin{cases} -1 \text{ for } |r| < \sigma \\ 0 \text{ for } |r| \geq \sigma. \end{cases} \qquad (A.22)$$

Both B_2 and B_3 have been computed analytically[17] for a gas of hard disks, and are

$$B_2 = \pi\sigma^2/2, \qquad (A.23)$$

$$B_3 = [(4/3) - (\sqrt{3}/\pi)](\pi\sigma^2/2)^2. \qquad (A.24)$$

The values for hard spheres are given by Eqs. (30a) and (30b). From these expressions we readily obtain the modified van der Waals expression for χ, as given by Eqs. (23) and (28) of the text. It is also possible to obtain the virial expansion for χ directly from its definition as the value of the radial distribution function at contact. Although we will not give the derivation here, it can be shown that for a one-component system, χ can be expressed in terms of Mayer f functions as

$$\chi = 1 + n \int dr_3 f(r_{13})f(r_{23}) |_{r_{12}=\sigma} + \cdots. \quad (A.25)$$

The notation on the integral means that the integration over r_3 is to be carried out under the condition that particles 1 and 2 are just touching, i.e., $|r_1 - r_2| = r_{12} = \sigma$, as shown in Fig. 4. An evaluation of this integral is not difficult for hard disks; indeed, it can be carried out by simple geometrical considerations, as was shown in the text in connection with Fig. 4.

To extend these ideas to treat mixtures of hard disks (or spheres) of various diameters, we need to have virial expansions for the various χ_{ij} factors. For our purposes we will need only the first two terms in the expansion. Thus, for a general binary mixture we only need to use

$$\chi_{ij} = 1 + \sum_{k=1}^{2} n_k \int dr_3 f_{ik}(r_{13})f_{kj}(r_{23})|_{r_{12}=\sigma_{ij}} + \cdots, \qquad (A.26)$$

where the sum over k runs over the two species, with number densities n_1 and n_2, respectively, and f_{ik} is defined by

$$f_{ik}(r_{13}) = e^{-\beta V_{ik}(r_{13})} - 1, \qquad (A.27)$$

in which $V_{ik}(r_{13})$ is the interaction potential between a particle of species i and one of species k. A simple modified van der Waals expression for χ_{ij} would then be

$$(\chi_{ij})_{\text{vdW}}^{\text{mod}} = \left[1 - \sum_k n_k \int d\mathbf{r}_3 f_{ik}(r_{13}) \right.$$

$$\left. \times f_{kj}(r_{23}) \Big|_{r_{12}=\sigma_{ij}} \right]^{-1}. \quad (A.28)$$

It is tempting to try to improve this formula by using a Padé approximant to incorporate some information about the behavior of χ_{ij} as the system becomes close packed. However, for a general mixture of hard disks (or spheres), it is not always clear what the properties of the χ_{ij} will be at close packing, because of the way small particles can pack into the interstices between large particles, and it seems safer to stop with Eq. (A.28).

For the special mixture used in the air table experiments carried out in the freshman laboratory at the University of Maryland, we need only χ_{12}, the radial distribution function for the special disk called 1 in contact with one of the regular disks in the system denoted as species 2. The virial expansion of χ_{12} is then given by

$$\chi_{12} = 1 + n_2 \int d\mathbf{r}_3 f_{12}(r_{13}) f_{22}(r_{23}) \Big|_{r_{12}=\sigma_{12}} + \cdots, \quad (A.29)$$

where n_2 is the number density of the regular disks of the system. There is no summation in the second term of Eq. (A.29) because there is only one particle of species 1, so that all the excluded volume effects involve the one particle of species 1 with one or more particles of species 2. After performing the required integration we find that

$$\chi_{12} = 1 + n_2 h(r,R) + O(n_2^2), \quad (A.30)$$

where

$$h(r,R) = \frac{\pi}{2}(R^2 + r^2) - R^2 \arcsin\left(1 - \frac{r^2}{2R^2}\right)$$

$$- r^2 \arcsin\left(\frac{r}{2R}\right) - rR\left(1 - \frac{r^2}{4R^2}\right)^{1/2}, \quad (A.31)$$

and

$$R = \sigma_{12} = \tfrac{1}{2}(\sigma_1 + \sigma_2), \qquad r = \sigma_2. \quad (A.32)$$

One can easily verify that as $R \to r$,

$$h(r,R) \to (\pi r^2/2)\,[(4/3) - (\sqrt{3}/\pi)]. \quad (A.33)$$

The modified van der Waals expression for χ_{12} is thus

$$(\chi_{12})_{\text{vdW}}^{\text{mod}} = [1 - n_2 h(r,R)]^{-1}. \quad (A.34)$$

This is the result used in analyzing a typical experiment in the freshman laboratory, where the marked puck is larger than the other pucks.

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