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Ion Clustering*

STANLEY BLOOM AND HENRY MARGENAU
Sloane Physics Laboratory, Yale University, New Haven, Connecticut

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Kinetic theory is employed in investigating the extent to which polarizable molecules attach themselves to slowly moving ions in a gas, the underlying picture being that commonly used in deriving the barometric equation, i.e., the aggregation of molecules in a constant field of force. A potential energy of the form $-\kappa r^{-4}$ for $r \geqslant r_0$ but ∞ for $r \leqslant r_0$, leads to a large cluster formation. This hard-sphere potential, however, packs most of the clustered molecules into the sharp crevasse near r_0 and therefore falsifies the result. When the cusp is removed by the more adequate potential $\lambda r^{-12} - \kappa r^{-4}$, the tendency to cluster is reduced nearly 100-fold. Results are obtained in general agreement with experiment, except for $\mathrm{Li}^+ - \mathrm{Kr}$, where theory predicts a much smaller cluster than that inferred from mobility measurements.

I. INTRODUCTION

A SIMPLE approach to the problem of ion clustering is given by Loeb.[1] As this author himself has recognized, and as is emphasized in his forthcoming book, this schematic treatment makes no allowance for the statistical weights of different states of motion of the ion-molecule system. More elaborate calculations,[2] on the other hand, introduce complications which the problem hardly possesses, for they fashion it after the theories of molecular dissociation and take explicit account of quantization.

Whether or not this is necessary depends primarily on the spacing of the energy levels in the potential trough describing the interaction between ion and molecule. If it is narrow and the number of levels is small, quantum effects are certainly important. Otherwise classical statistics may be applied. Computations made with simplified potentials show the latter alternative to prevail. The number of vibrational levels is of the order of 50 in all interesting instances, though for the case of H_2 interacting with Li^+ it is but 10 (because of the small mass of these systems). We are therefore entitled to attack the clustering problem in the spirit of classical kinetic theory. The work will be limited to simple nonpolar gases. The underlying picture is that commonly used in deriving the barometric equation, i.e., the aggregation of molecules in a constant field of force.

II. THEORY

A. Hard-Sphere Repulsion

Let $V(r)$ be the potential energy of a neutral molecule at a distance r from the center of the ion. The number of molecules with velocity near v and contained in a spherical shell of radius r is

$$d^2N = Ar^2 dr v^2 dv \exp[-(V+\tfrac{1}{2}mv^2)/kT]. \tag{1}$$

The number within the spherical shell having any velocity, obtained by integrating d^2N over v, is

$$dN = (\pi^{\frac{1}{2}}/4\beta^3) Ar^2 dr \exp(-V/kT)$$

where $\beta^2 \equiv m/2kT$. Now consider a spherical container of volume $\tau = (4\pi/3)(R^3 - r_0^3)$ containing N_0 molecules. Then

$$N_0 = (\pi^{\frac{1}{2}}/4\beta^3) A \int_{r_0}^{R} dr r^2 \exp(-V/kT), \tag{2}$$

r_0 being the distance of closest approach of ion and molecule. This relation determines the constant A. We wish to find the number N_B of bound molecules, i.e., those whose total energy is negative:

$$V(r) + \tfrac{1}{2}mv^2 \leqslant 0. \tag{3}$$

In this first part of the analysis, the ion and molecule will be considered as exhibiting a "hard-sphere" repulsion. The attraction considered here is that arising between the ion and the ion-induced dipole moment on the molecule; other effects will first be neglected. The potential energy is then given by

$$\begin{aligned} V(r) &= -\kappa r^{-4}, \quad r \geqslant r_0 \\ &= \infty, \qquad\quad r \leqslant r_0 \quad \text{(see Fig. 1).} \end{aligned} \tag{4}$$

The clustering criterion (3) is therefore

$$v \leqslant (2\kappa/m)^{\frac{1}{2}} r^{-2} = \alpha^{\frac{1}{2}}/\beta r^2, \tag{5}$$

where $\alpha \equiv \kappa/kT$. From Eq. (1) we obtain

$$N_B = 4N_0 \beta^3 \pi^{-\frac{1}{2}} \times \frac{\int_{r_0}^{R} r^2 \exp(\alpha/r^4) dr \int_0^{\alpha^{\frac{1}{2}}/\beta r^2} v^2 \exp(-\beta^2 v^2) dv}{\int_{r_0}^{R} r^2 \exp(\alpha/r^4) dr}. \tag{6}$$

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[*] Assisted by the ONR.

[1] L. B. Loeb, *Fundamental Processes of Electrical Discharge in Gases* (John Wiley and Sons, Inc., New York, 1939). Taking all molecules to have the mean thermal velocity, Loeb describes clustering in terms of a region of stability about the ion. His criterion for clustering is $-V(r) \geqslant \frac{1}{2}m\langle v^2 \rangle_{\mathrm{Av}}$, which gives a radius $r_{\max}$, beyond which a molecule remains free. The number of clustered molecules is then taken to be that which can be close-packed into a sphere of radius $r_{\max}$.

[2] Eyring, Hirschfelder, and Taylor, J. Chem. Phys. **4**, 479 (1936). For a discussion of the influence of clustering on ion mobilities in mixed gases, see A. W. Overhauser, Phys. Rev. **76**, 250 (1949).

The numerator of this expression is

$$2N_0\pi^{-\frac{1}{2}}\int_{r_0}^{R} r^2\exp(\alpha/r^4)\Gamma(\tfrac{3}{2},\alpha/r^4)dr$$

provided we introduce the incomplete Γ-function

$$\Gamma(\tfrac{3}{2},y)=\int_0^y dxe^{-x}x^{\frac{1}{2}}.$$

If we write the denominator in the form

$$\tfrac{1}{3}(R^3-r_0^3)+\int_{r_0}^{R} drr^2[\exp(\alpha/r^4)-1]$$

we see that both r_0^3 and the integral are negligible against R^3 as $R\rightarrow\infty$. The number density $n_0=N_0/\tau$, hence in the limit as $R\rightarrow\infty$

$$N_B=8n_0\pi^{\frac{1}{2}}\int_{r_0}^{\infty} drr^2\exp(\alpha/r^4)\Gamma(\tfrac{3}{2},\alpha/r^4)$$

$$=2n_0\pi^{\frac{1}{2}}\alpha^{\frac{3}{4}}\int_0^b dxe^{x}x^{-7/4}\Gamma(\tfrac{3}{2},x), \tag{7}$$

where $b\equiv\alpha/r_0^4$. For convenience we write this in the form

$$N_B/2n_0r_0^3\pi^{\frac{1}{2}}=b^{\frac{3}{4}}\int_0^b dxe^{x}x^{-7/4}\Gamma(\tfrac{3}{2},x)\equiv Q(b). \tag{8}$$

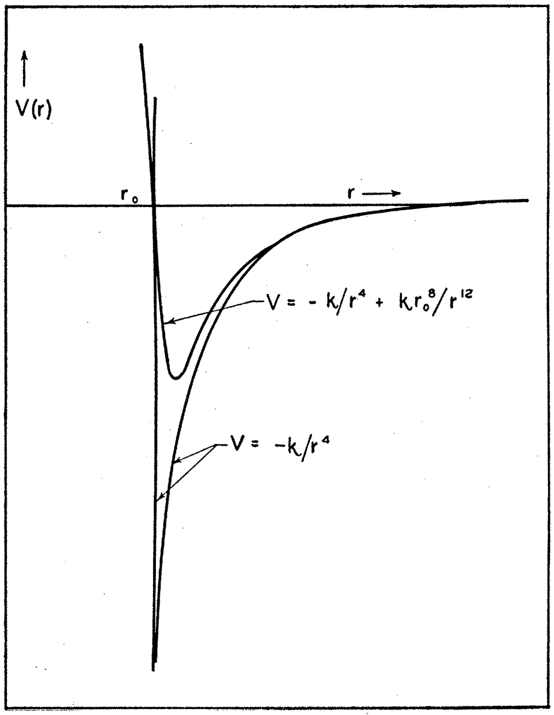

FIG. 1. Potential energy $V(r)$ *vs* r (schematic).

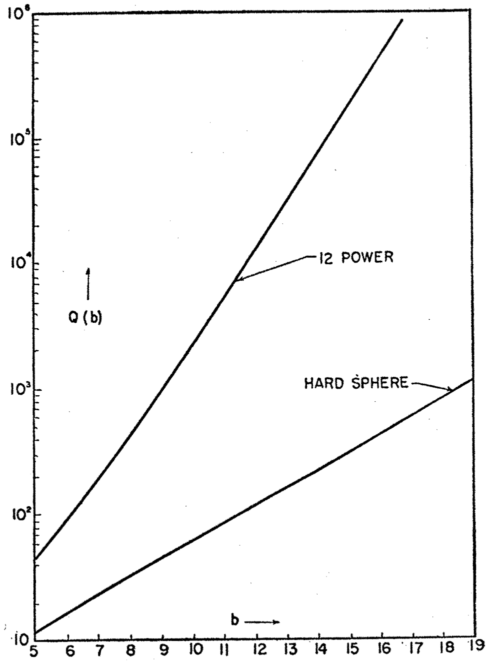

FIG. 2. $Q(b)$ *vs* b. [See Eqs. (8) and (17).]

Because of the divergence of the integrand at $x=0$, the integration is split into two parts:

$$Q(b)/b^{\frac{3}{4}}=\int_0^{\epsilon}+\int_{\epsilon}^{b}\equiv K''+K'. \tag{9}$$

ϵ was chosen to be $0.6\sqrt{\frac{3}{2}}$, which is a convenient value. K'' is found by series expansion of the integrand; it is

$$K''=0.807. \tag{10}$$

The integral

$$K'=\int_{0.6(\frac{3}{2})^{\frac{1}{2}}}^{b} dxe^{x}x^{-7/4}\Gamma(\tfrac{3}{2},x)$$

is computed by numerical quadrature. Figure 2 represents $Q(b)$ *vs* b.

It is to be noted that our analysis treats the ion as stationary and the molecule as having the velocity v. If the calculation is made in terms of relative velocities, as it should be, the only effect on the preceding formulas is the replacement of the molecular mass by the reduced mass. This appears in $\beta=(m/2kT)^{\frac{1}{2}}$, which drops out from our equations, indicating that they will not change when the ion is allowed to have its own temperature motion.

To obtain N_B for specific systems we must know κ, the force law constant, and r_0, the distance of closest approach of ion and molecule. Neither is known accurately, and indeed r_0 is not a well-defined concept. For κ we shall use the dielectric law of attraction,

$$\kappa=(D-1)e^2/8\pi L \tag{11}$$

where L is the Loschmidt number and D is the dielectric

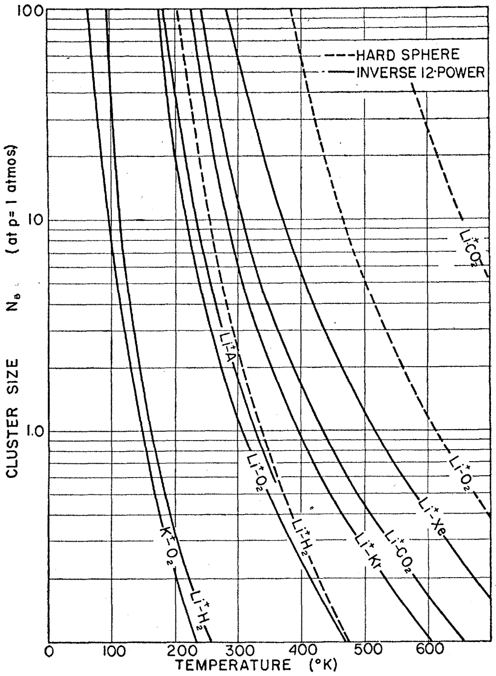

FIG. 3. Cluster size N_B *vs* temperature, at 1 atmosphere.

constant of the molecule. This, of course, is an approximation since Eq. (11) is derived for low uniform fields. As Loeb[1] points out, experimental values for the dielectric constant lead to values of κ which are probably 10 to 20 percent too high. However, in view of our neglect of Van der Waals attractions, which would give higher effective values of κ, there seems little point in attempting to improve upon Eq. (11).[3] A more serious difficulty arises in connection with r_0, since it enters in a more sensitive way into the formulas. We have taken Margenau's[3] values which are the sum of the radii of ion and molecule.

Figure 3 gives the resulting values of N_B at various temperatures for some representative ion-molecule systems. The numerical constants used are given in Table I. Since N_B is proportional to the number density, we have arbitrarily kept n_0 fixed at $2.687(10^{19})$ per cm^3, the value for 0°C and 1 atmosphere.

Figure 3 shows that at room temperature and a pressure of one atmosphere, the present model leads to appreciable clustering in all cases considered. This is due, as we shall now show, to the presence of the deep crevasse in the hard-sphere model. (See Fig. 1.)

B. Inverse 12-Power Repulsion

We shall now take as the potential energy

$$V(r)=\lambda r^{-12}-\kappa r^{-4}. \tag{12}$$

The analysis proceeds as before, the criterion for clustering being $v\leqslant(-2V/m)^{\frac{1}{2}}\equiv v_m$, for $V\leqslant 0$. This gives

$$N_B=16n_0\beta^3\pi^{\frac{1}{2}}\int_{r_1}^{\infty}drr^2e^{-V/kT}\int_0^{v_m}dvv^2\exp(-\beta^2v^2). \tag{13}$$

Here r_1 is defined by the relation

$$V(r_1)=0,\quad\text{or}\quad r_1=(\lambda/\kappa)^{1/8}. \tag{14}$$

Integration over v results in

$$N_B=8n_0\pi^{\frac{1}{2}}\int_{r_1}^{\infty}drr^2\exp(\alpha r^{-4}-\gamma r^{-12})\times\Gamma(\tfrac{3}{2},\,\alpha/r^4-\gamma/r^{12}) \tag{15}$$

provided we write $\alpha=\kappa/kT$, $\gamma=\lambda/kT$. Since the force-law constant γ is not known, we shall replace r_1 by the hard-sphere value r_0 previously used. Then $\gamma=\alpha r_0^8$ and

$$N_B=8n_0\pi^{\frac{1}{2}}\int_{r}^{\infty}drr^2\exp[(1-r_0^8/r^8)\alpha/r^4]\times\Gamma[\tfrac{3}{2},\,(1-r_0^8/r^8)\alpha/r^4]. \tag{16}$$

This integral can be put into a more convenient form by the substitution $y=r_0^4/r^4$. Then

$$N_B=2n_0r_0^3\pi^{\frac{1}{2}}\int_0^1dyy^{-7/4}\exp[by(1-y^2)]\times\Gamma[\tfrac{3}{2},\,by(1-y^2)] \tag{17}$$

where, as before, $b\equiv\alpha r_0^{-4}$. The integral

$$N_B/2n_0r_0^3\pi^{\frac{1}{2}}\equiv Q(b) \tag{18}$$

is evaluated numerically for various values of b. Because of the divergence of the integrand as $y\rightarrow 0$, it is again necessary to take

$$Q(b)=\int_0^{\epsilon}+\int_{\epsilon}^{1.0}\equiv P(b)+M(b).$$

(Here $\epsilon=0.01$ is used.) The integral $P(b)$ is obtained

TABLE I. Constants of ion-molecule systems.

	Dielectric constant $(D-1)$ $\times 10^4$	Force constant $\kappa\times 10^{44}$ erg-cm^4			r_0(A)[a]		
			Li$^+$	Na$^+$	K$^+$	Rb$^+$	Cs$^+$
H_2	2.64[b, c]	9.014	2.16	2.36	2.71	2.87	3.03
O_2	5.43[c]	18.54	2.23	2.43	2.78	2.94	3.10
CO_2	9.85[b]	33.62	2.39	2.59	2.94	3.10	3.26
A	5.68[c]	19.39	2.21	2.41	2.76	2.92	3.08
Kr	8.50[c]	29.02	2.35	2.55	2.90	3.06	3.22
Xe.	13.78[c]	47.05	2.49	2.69	3.04	3.20	3.36

[a] H. Margenau, reference 3.
[b] *Handbook of Chemistry and Physics* (Chemical Rubber Publishing Company).
[c] J. Jeans, *The Dynamical Theory of Gases* (Cambridge University Press, London, 1925).

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[3] H. Margenau, Philosophy of Science 8, 603 (1941). In this paper values are given of the interaction energy between various ions and foreign molecules at the distance of closest approach, with and without Van der Waals' forces.

by series expansion and $M(b)$ by numerical quadrature. Figure 2 gives the values of $Q(b)$ for the case of the 12-power law. Extrapolation was used to extend the plot of $Q(b)$ to the larger values of b. It is seen that $Q(b)$ is nearly an exponential function of b on both models. With these values of $Q(b)$ we obtain the results for N_B shown in Fig. 3.

It is seen that the inclusion of the "soft" repulsion reduces the number of clustered molecules by a factor greater than 100. At 273°K and a pressure of one atmosphere the highly polarizable CO_2 molecules form a cluster about a Li^+ ion of about 28 molecules. Oxygen, with intermediate polarizability, "clusters" to the extent of only 2 molecules, and H_2, with very low polarizability, has an N_B of about 0.08—i.e., no clustering. The alkali ions in order of increasing radii are Li^+, Na^+, K^+, Rb^+, and Cs^+, so that Li^+ is the strongest clustering agent. Figure 3 shows N_B for K^+-O_2; at normal temperature and pressure, N_B has the negligible value of about 0.05.

The present calculations are incomplete inasmuch as they neglect interactions between clustering molecules, which are treated as points. In other words, no account has been taken of steric exclusion. This could be introduced in qualitatively satisfactory fashion by supposing that, whenever the present theory gives a number of clustered molecules greater than can be packed into the surrounding space considered by Loeb, it must be reduced to that number. At any rate, it is clear that steric effects reduce the clusters here computed. Since we have shown that clustering is a rare phenomenon even on the present basis, the steric refinement seems unimportant.

A rough idea of the spatial distribution of those few molecules that might cluster can be had from the fact that in Eq. (17) the contribution to the integral from $y=0$ to $y=0.01$ is, for the important values of b, approximately 1 percent or less of that coming from the remaining range. But this small interval in y corresponds to the large interval in r between $(10)^{\frac{1}{2}}r_0$ and ∞. In other words, roughly 99 percent of the molecules that do cluster congregate within a distance of about $3.2r_0$ from the ion.

III. COMPARISON WITH EXPERIMENT

Munson and Hoselitz,[4] in their measurements of the mobilities of alkali ions in inert gases, present some data on clustering. They find that only Li^+ can serve as a clustering agent and that the greater the atomic weight of the rare gas atom (and, therefore, the greater its polarizability) the higher the temperature at which it may form a cluster with the lithium ion. An attempt was made to observe a cluster with K^+ in argon. This was unsuccessful even at the relatively low temperature of 126°K. On the other hand, Li^+ in argon readily formed clusters at 195°K. Table II gives Munson and Hoselitz's experimentally deduced values for the cluster sizes.

TABLE II. Experimental and theoretical values of N_B.

System	Temp. (°K)	N_B Experiment[a]	N_B Theory (at $p=19$ mm of Hg)
Li^+-A	195	2	1.7
Li^+-Xe	290	2	2.3
Li^+-Kr	290	2	0.2
Li^+-Kr	225	...	$\sim$2

[a] See reference 4.

Unfortunately, Munson and Hoselitz do not give values for the pressures they used. The last column in Table II gives our calculated N_B for the pressure $p=19$ mm Hg, which is of the order of magnitude of the pressures usually employed in mobility experiments of this kind.

It is seen that for the cases of Li^+ in argon and xenon, our N_B is comparable to the experimentally deduced values. However, in the case of krypton, we obtain $N_B \simeq 0.2$, i.e., negligible clustering, whereas experiment seems to yield the value of 2 at the temperature $T=290$°K. In order for our analysis to give $N_B=2$ at $p=19$ mm Hg, we would have to lower the temperature to 225°K; or keeping $T=290$°K, the pressure would have to be raised to as much as 190 mm Hg. Lacking information as to the experimental pressures, it is difficult to understand this apparently discrepant result for Li^+-Kr. Munson and Hoselitz's indication of two clustered atoms for both Xe and Kr on Li^+ at the same temperature does seem strange, however. Xenon has a force constant (proportional to the polarizability) of $\kappa=47\times10^{-44}$ erg cm^4, and with Li^+, $r_0=2.49$A. Now, even though the distance of closest approach r_0 for Li^+-Kr is less than that for Li^+-Xe, the fact that κ for Xe is 1.6 times as large as that for Kr far outweighs the difference in the r_0 values. Hence Xe should be more clusterable than Kr.

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[4] J. R. Munson and K. Hoselitz, Proc. Roy. Soc. (London) A172, 43 (1939).