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THEORY OF INTERMOLECULAR INTERACTION AND EQUATION OF STATE OF AN EXCITED GAS

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We consider the thermodynamic functions and the equation of state of a gas in which there is maintained a well-defined number of atoms in a stationary state excited to the same electron energy level. We take into account the resonance dipole-dipole interaction only between atoms with different electron energies. We develop a kind of virial expansion in powers of the small concentration of excited atoms for arbitrary concentrations of the non-excited atoms. The higher-order cluster integrals, up to and including quadrupole collisions, are taken into account. We discuss the possibility that the gas may split into two spatially separated phases with different relative contents of excited atoms.

THE authors have shown earlier[1] that the resonance dipole-dipole interaction between molecules in different energy levels, which is proportional to the inverse cube of the distance between them, may contribute to the thermodynamic functions of the gas to an appreciably larger degree than the usual van der Waals forces. Even for a small relative amount of excited molecules in the gas (5 to 10%), this resonance interaction leads to a large deviation from the ideal gas behavior under conditions for which the unexcited gas would be almost ideal.

We considered an atomic gas in which a well-defined number of atoms was excited in a stationary state to one single energy level by means of a light source or some other pumping mechanism. We evaluated for such a gas the thermodynamic functions and the equation of state in the framework of the usual theory of weakly imperfect gases.[2] We then took into account only the interaction between excited and non-excited atoms in the binary collision approximation.

On the basis of an extrapolation of the equation of state in the region of large deviations from perfect behavior, similar to what is usually done to give a theoretical basis for the van der Waals equation (see[2]), we noted in[1] the possibility of a thermodynamic instability and of the splitting of an excited gas into two phases with different relative contents of excited atoms and subsequent condensation of one of the phases.

The equation of state of the gas, obtained through the extrapolation of the theory beyond the framework in which it is applicable, is always doubtful. One must thus try to generalize it to the region of larger concentrations and deviations from perfect behavior. Such an attempt was made by Vdovin[3], who obtained an equation of state valid for larger deviations from perfect behavior than the corresponding equation in[1] and arrived at the conclusion that a spatially uniform excited gas is thermodynamically unstable.

However, this conclusion was based upon an equation of state which nevertheless took into account only binary collision cluster integrals. This equation is therefore inapplicable to concentrations that are so large (atmospheric pressure) that their possible instability was noted in[1].

To consider the region of those concentrations, one of the authors generalized in a later paper[4] the quantum cluster expansion method of Kahn and Uhlenbeck[5] to the case of a gas consisting of two kinds of atoms (excited to two different energy levels). As a result the equation of state of the gas was obtained by eliminating the parameters ξ and ξ' from the following three equations:

$$p=\sum_{ll'} b_{ll'}\xi^{l}\xi'^{l'},$$

$$n=\sum_{ll'} l b_{ll'}\xi^{l}\xi'^{l'},\quad n'=\sum_{ll'} l' b_{ll'}\xi^{l}\xi'^{l'}. \tag{1}$$

Here n and n′ are the concentrations of the atoms with, respectively, electron energies ϵ and ϵ'; $b_{ll'}$ are the cluster integrals which, when we take into account only resonance dipole-dipole interactions between atoms in different states of excitation, have the form $b_{10} = b_{01} = 1$, $b_{l0} = b_{0l'} = 0$, $l, l' > 1$;

$$b_{11}=\frac{1}{2!gg'V}\int dR_a\,dR_b\sum_{s_{11}}[E_{s_{11}}-1],$$

$$b_{21}=\frac{1}{3!g^2g'V}\int dR_a\,dR_b\,dR_c\Big\{\sum_{s_{21}}[E_{s_{21}}-1]-3g\sum_{s_{11}}[E_{s_{11}}-1]\Big\},$$

$$\begin{aligned}b_{22}=\frac{1}{4!g^2g'^2V}\int dR_a dR_b dR_c dR_d\Big\{&\sum_{s_{22}}[E_{s_{22}}-1]-4g\sum_{s_{12}}[E_{s_{12}}-1]\\&-4g'\sum_{s_{21}}[E_{s_{21}}-1]-6\sum_{s_{11}}[E_{s_{11}}(R_aR_b)-1]\cdot\\&\cdot\sum_{s_{11}}[E_{s_{11}}(R_cR_d)-1]-12(g+g'+gg')\sum_{s_{11}}[E_{s_{11}}-1]\Big\},\end{aligned} \tag{2}$$

$$b_{ll'}=b_{l'l}.$$

The indices l and l' of $b_{ll'}$ are the number of atoms with energies ϵ and ϵ' in the cluster of $l + l'$ adjacent interacting atoms,

$$E_{s_{ll'}}(R_a,R_b,\ldots)=\exp\{-W_{s_{ll'}}(R_a,R_b,\ldots)/T\},$$

$W_{s_{ll'}}(R_a, R_b, \ldots)$ is the potential energy of the nuclei of the $l + l'$ adjacent atoms; $R_a, R_b, \ldots$ are the coordinates of these nuclei, $s_{ll'}$ the set of quantum numbers determining the state of the cluster of $l + l'$ adjacent atoms; g and g′ the degrees of degeneracy of the levels ϵ and ϵ', respectively; V the volume of the gas; T the absolute temperature multiplied by Boltzmann's constant. See[4] for a definition of the $b_{ll'}$ with larger values of l and l'. We note that all cluster integrals have the following properties: they vanish as soon as one of the particles of the cluster of $l + l'$ adjacent particles goes to infinity.

In the following we shall use Eqs. (1) and (2) to obtain an equation of state of a resonance excited gas for the case $n' \ll n$. The solution of Eq. (1), using the method of successive approximations assuming that n and n′ are quantities of first order of smallness, leads to the following equation of state:

$$\begin{aligned} p = T[n + n' - b_{11}nn' + (b_{11}^2 - 2b_{21})(n^2n' + nn'^2) \\ - (b_{11}^3 - 3b_{21}b_{11} + 3b_{31})(n^3n' + nn'^3) \\ - 3(b_{11}^3 - 2b_{21}b_{11} + b_{22})n^2n'^2 + \ldots]. \end{aligned} \tag{3}$$

This virial expansion converges well, provided

$$b_{11}n \ll 1, \quad b_{11}n' \ll 1. \tag{4}$$

One can, however, solve Eq. (1) assuming that only one of the concentrations, e.g., n′, is a first-order small quantity, while there is no restriction on the value of n. We then get a virial expansion in powers of n′ only. It has the form

$$p = T[n + \alpha n' + \beta n'^2 + \gamma n'^3 + \ldots], \tag{5}$$

$$\alpha = (1 + A_1 - B_1) / (1 + A_1),$$

$$\beta = \frac{B_1B_1' - A_2B_2 + A_1B_1B_1' - A_1A_2 - A_1B_2 - B_1^2A_1' + 2B_1A_2}{(1 + A_1)^3},$$

$$\gamma = \frac{B_1B_2' - B_1'(B_1B_2' - B_2) - 2A_3 - B_3}{(1 + A_1)^3} + \frac{2(B_1A_1' - 2A_2)(B_1B_1' - B_2 - A_2)}{(1 + A_1)^4}$$
$$+ \frac{B_1[A_1'(B_1B_1' - B_2) - B_1A_2' + 3A_3]}{(1 + A_1)^4} - \frac{2B_1(B_1A_1' - 2A_2)^2}{(1 + A_1)^5},$$

$$A_i = \sum_{l=1}^{\infty} b_{li}n^l, \quad B_i = \sum_{l=1}^{\infty} lb_{li}n^l, \quad A_i' = \frac{dA_i}{dn}, \quad B_i' = \frac{dB_i}{dn}.$$

We note that the equation of state (5) can be applied also to a gas mixture consisting of two kinds of excited atoms, provided only the interaction between molecules of a different kind is important.

Usually the complexity of evaluating the cluster integrals $b_{ll'}$ increases rapidly with increasing l and l'. It is therefore practically possible to determine the $b_{ll'}$ only for very small l, l'. For instance, in[1] we determined only b_{11} which corresponds to taking only binary collisions between equally-excited atoms into account. In that case we noted, however, the important difference of the resonance interaction (inversely proportional to the cube of the distance between the atoms) and the usual van der Waals forces which means that ternary and higher-order collisions play a relatively less important role than binary ones.

Estimates in[3] as well as our own estimates show that if

$$l > 1, \quad b_{1l} \gg b_{l1}.$$

The value of b_{11} therefore allows us in the expansion (3) to determine not only the usual term in the theory of weakly imperfect gases, which is proportional to nn', but also terms proportional to n^2n', nn'^2, n^3n', nn'^3.

Turning to the equation of state (5) we can write it down taking into account the binary cluster integrals b_{11}, the ternary cluster integrals $b_{21} = b_{12}$, and from the fourth-order cluster integrals we take into account only the most important one b_{22}. It is possible to neglect the other cluster integrals if n satisfies the inequalities

$$b_{l1}n^{l-1} \ll b_{11}, \quad b_{l2}n^{l-2} \ll b_{22}, \ldots, l > 2. \tag{6}$$

In that case (5) becomes

$$\begin{aligned} p = T\{n + n'(1 - b_{21}n^2)\Delta \\ + n'^2[(b_{11}^2 - 2b_{21})n + 3(2b_{21}b_{11} - b_{22})n^2 \\ + (10b_{21}^2 + b_{21}b_{11}^2 - b_{22}b_{11})n^3 + b_{21}|2b_{21}b_{11} + b_{22})n^4]\Delta^3 + \ldots\}, \\ \Delta = 1 / (1 + b_{11}n + b_{21}n^2). \end{aligned} \tag{7}$$

If we restrict ourselves in (7) to the terms linear in the concentration of the excited atoms, we get an equation of state which is the same as the corresponding result from Vdovin's paper.[3] Explicit expressions for b_{11} were given in[1] and for b_{21} in[4]. We make a rough estimate for b_{22}:

$$b_{22} \sim r_0^9 \left(\frac{T}{|W_{min}|}\right)^3 \exp\left\{-\frac{W_{min}}{T}\right\}, \quad \frac{|W_{min}|}{T} \gg 1, \tag{8}$$

where r_0 is the closest possible distance between the center of atoms for which there are infinite repulsive forces between them (atom diameter)[1], W_{min} is the smallest value of the potential interaction energy of a quadrupolet of atoms at the closest possible distance of which two atoms are excited (in the dipole-dipole approximation). For a linear chain of four atoms the dipole-dipole interaction energy is, when we take the interaction between all atoms into account, equal to $W \approx -4.85\,A/r_0^5$ where A is the absolute square of the matrix element of the dipole moment transition from the S-state which is the ground state to the P-state considered. It is possible that for other configurations of four atoms in contact we would have obtained a larger bound energy. We may thus assume that

$$W_{min} \leqslant -4.85\,A / r_0^3. \tag{9}$$

We can easily solve the equation of state (7) for the volume:

$$\begin{aligned} V = N_0\left[\frac{T}{p} + xV_1 + x^2V_2 + \ldots \right. ; \\ x = \frac{n'}{n + n'}, \quad V_1 = -\left(b_{11} + b_{21}\frac{p}{T}\right)\Delta, \\ V_2 = \left[b_{11} + (b_{11}^2 + 2b_{21})\frac{p}{T} + 3(2b_{21}b_{11} - b_{22})\frac{p^2}{T^2}\right. \\ \left. + (6b_{21}^2 + b_{21}b_{11}^2 - b_{22}b_{11})\frac{p^3}{T^3} + b_{21}(b_{21}b_{11} + b_{22})\frac{p^4}{T^4}\right]\Delta^3. \end{aligned} \tag{10}$$

We can use (10) to determine the thermodynamic potential Φ (p, T, x) as an integral of V(p, T, x) over p. The arbitrary integration constant c(T, x) can then be found from the condition: as $p \to 0$, the thermodynamic potential $\Phi(p, T, x) \to N_0T[x \ln x + (1 - x) \ln \times (1 - x) + \ln p]$, which is the thermodynamic potential of the mixture of two perfect gases. As a result, when we take binary, ternary, and the quaternary cluster integrals b_{22} into account, $\Phi(p, T, x)$ takes the form

$$\Phi = N_0T\Big\{x\ln x + (1-x)\ln(1-x) + \ln p - x\ln\Delta + 2x^2 - x^2\Big[2 + 3b_{11}\frac{p}{T} + b_{11}{}^2\frac{p^2}{T^2} + (b_{21}b_{11} + b_{22})\frac{p^3}{T^3}\Big]\Delta^2 + \ldots\Big\}. \quad (11)$$

(To get (11) we have bore in mind that $b_{11}^2 \gg b_{21}$.) At not too large a concentration n when the inequalities

$$b_{21}n^2 \ll 1,\quad b_{22}n^2 \ll b_{11},\quad b_{21}n \ll b_{11}, \quad (12)$$

are satisfied we can drop in the expansions (3) and (7) all cluster integrals bar b_{11}. In that case the series simplify and they can be summed. We are then led to the equation of state first obtained in[3] by Vdovin by a different method:

$$p = {}^1\!/_2T\{n + n' + b_{11}{}^{-1}[\sqrt{(1 + b_{11}n + b_{11}n')^2 - 4b_{11}{}^2nn'} - 1]\}. \quad (13)$$

It is an interesting result to have the possibility to obtain the equation of state in closed form (13) instead of as a virial expansion (even in a limited range of concentrations); this result is the consequence of the specific nature of the resonance dipole-dipole interaction: the pair collisions cluster integral b_{11} has an anomalously large relative magnitude.

Using (13), it was noted correctly in[3] that $\partial^2\Phi/\partial x^2 > 0$ for all x, i.e., the excited gas is stable against a splitting up into two phases.

However, this conclusion, as also Eq. (13), is valid only for concentrations limited by inequalities (12). For instance, the first of them compels us to restrict ourselves to concentrations of the order of 10^{17} cm^{-3}. To study the thermodynamic stability of the gas at higher concentrations of 10^{19} to 10^{21} cm^{-3}, which are permissible under inequalities (6), we turn to Eq. (11). It follows from this that

$$\frac{\partial^2\Phi}{\partial x^2} \approx N_0T\Big\{4 + \frac{1}{x(1-x)} - 2\Delta^2\Big[2 + 3b_{11}\frac{p}{T} + b_{11}{}^2\frac{p^2}{T^2} + \frac{p^3}{T^3}(b_{21}b_{11} + b_{22})\Big]\Big\}. \quad (14)$$

For concentrations satisfying the relations

$$b_{21}n^2 \gg 1,\quad b_{11}n \gg 1, \quad (15)$$

a splitting into two phases with different relative contents of excited atoms would be possible ($\partial^2\Phi/\partial x^2 < 0$), provided

$$b_{22} \gg b_{11}b_{21}. \quad (16)$$

This inequality has not yet been discussed in the literature. If we take the right-hand side of this inequality from[1,4] and the left-hand side following the rough estimate (8) we can rewrite it in the form

$$\left(\frac{T}{|W_{min}|}\right)^3 \exp\left\{-\frac{W_{min}}{T}\right\} \gg \frac{4\pi^3}{243\sqrt{3}}\left(\frac{r_0{}^3T}{A}\right)^{7/2} \exp\left\{\frac{5A}{r_0{}^3T}\right\}. \quad (17)$$

For the values of the parameter $A/r_0^3T \sim 10$, taken in[1,4] this inequality starts being valid when $W_{min} < -5.3\ A/r_0^3$. In that case a splitting of the excited gas into two spatially separated phases would be possible already for rather small x in the region where the equation of state (7), which was obtained without the above mentioned extrapolation, is valid. To check this statement it is necessary to evaluate b_{22} more exactly.

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