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THE SECOND VIRIAL COEFFICIENT FOR A SYSTEM WITH RESONANCE TRANSFER OF ATOMIC EXCITATION

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The contribution made to the thermodynamic functions of a gas by resonance scattering of atoms, some of which are excited by an external agent (for example, a source of resonance light), is investigated. It is shown that under normal conditions such a system is essentially nonideal, so that the second virial coefficient is three orders of magnitude larger than that for an equivalent elastic-sphere system.

1. Let us consider a gas consisting of atoms in their ground state and atoms of the same kind in an excited state connected with the ground state by an allowed dipole transition. A stationary population in the excited state can be maintained in the system by a resonance light source, for example. If the concentration of excited atoms is not too small, the main contribution to the interaction energy of the system is due to the strong dipole-dipole interaction of excited and unexcited atoms. The resonance dipole-dipole interaction gives a nonvanishing contribution to the interaction energy in first-order perturbation theory, whereas in an ordinary van-der-Waals gas this contribution appears in second-order perturbation theory. Owing to this the cross section for resonance scattering of the atoms is rather large both in the elastic-scattering channel:

$$A_1' + A_2 \rightarrow A_1' + A_2, \tag{1}$$

and in the channel for resonance transfer of excitation by collision:

$$A_1' + A_2 \rightarrow A_1 + A_2', \tag{2}$$

where the prime corresponds to the excited state of the atom. For example, at normal temperature the cross section for resonance scattering of hydrogen atoms ($2p \rightarrow 1s$) is $\sigma = 3.1 \times 10^{-13}$ cm^2.[1]

Since the approximation of the system to a thermodynamically ideal gas depends on the ratio of the scattering amplitude to the mean distance between particles, we can expect a considerable contribution from the resonance scattering to the thermodynamic functions of this system. We note that the system is not in thermodynamic equilibrium, since the population of the excited state is fixed by the external source and is not determined by the Gibbs distribution. Therefore in the general case it is not legitimate to calculate the trace of a density matrix of the form $\exp\{-\hat{H}/T\}$. However, if there is time for equilibrium of the relative motion of the atoms to be established in the system, a thermodynamic description of this system is possible. We shall here deal with this case and take into account the contribution of the scattering of the atoms to the thermodynamic functions of the system, since the "collision time" $\tau \sim \sigma^{1/2}/v \approx 10^{-12}$ sec, where v is the mean relative velocity of two atoms, is always much smaller than the lifetime of the excited state of an atom. If the formation of bound molecular or quasimolecular states is possible in the collision of excited and unexcited atoms, inclusion of these states in the partition function with the Boltzmann weight is scarcely justified, when the lifetime of the excited state of the atom is rather small. Therefore we confine ourselves to the consideration of systems in which formation of bound states certainly does not occur, and include only the contribution of the interaction to the thermodynamic functions in the continuous spectrum. Furthermore we shall assume that $T \ll E_{\text{exc}}$, so that the contribution of thermally excited states to the thermodynamic functions can be neglected. An example of such a system is a volume filled with mercury vapor located in the radiation field of a mercury lamp.

We note that estimates of the contribution of bound states to the thermodynamic functions of a system have been given previously,[2,3] but the interaction of the atoms in the continuous spectrum was neglected. If there are no bound states, it is this interaction that causes the deviation of the system from ideal properties.

2. To find the contribution of two-particle interactions to the thermodynamic functions it is necessary to calculate the second virial coefficient. We shall assume that the contribution of excited atoms is not too small. Then the main contribution to the nonideality of the system comes from the interaction of excited and unexcited atoms. Therefore in calculating the second virial coefficient we take only this interaction into account.

Since the scattering cross section is much larger than the geometrical cross section, the effective range of the interaction is rather large, and we can write for the interaction operator

$$\hat{U} = \frac{(\bar{\mathbf{d}}_1 \bar{\mathbf{d}}_2) R^2 - 3(\bar{\mathbf{d}}_1 \bar{\mathbf{R}})(\bar{\mathbf{d}}_2 \bar{\mathbf{R}})}{R^5}, \tag{3}$$

where $\mathbf{d}_{1,2}$ are the dipole moments of the atoms and $\mathbf{R}$ is the distance between them.

We note that the contribution of higher multipole terms to the interaction operator goes to zero, since by hypothesis the excited state of the atom is connected with the ground state by an allowed dipole transition.

For simplicity we hereafter assume that the dipole moments of the colliding atoms are directed along the vector $\bar{\mathbf{R}}$ (rotating atom approximation). The accuracy of this approximation has been discussed, for example, in [4]. The expression for the interaction operator then takes the form

$$\hat{U} = -\frac{2d_{1z}d_{2z}}{R^3}, \tag{4}$$

where d_{1Z} and d_{2Z} are the projections of the dipole moments along the axis connecting their nuclei.

In this case the wave function of the system of two atoms (excited and unexcited) can be put in the form

$$\psi = \psi_1(\mathbf{R})\varphi_{A1}'(r_1)\varphi_{A2}(r_2) + \psi_2(\mathbf{R})\varphi_{A1}(r_1)\varphi_{A2}'(r_2), \tag{5}$$

where $\psi_i(\mathbf{R})$ describes the motion of the nuclei in channels 1 and 2, and φ'_{Ai} and φ_{Ai} are the respective electronic wave functions for the ground and excited states of an atom.[1] It is readily seen that when we use (5) the original Schrödinger wave equation reduces to the following system of equations for the functions ψ_1 and ψ_2 (cf., e.g., [1]):

$$(\hat{T} - \varepsilon_1)\psi_1 + \frac{|a|}{R^3}\psi_2 = 0, \quad (\hat{T} - \varepsilon_2)\psi_2 + \frac{|a|}{R^3}\psi_1 = 0, \tag{6}$$

where

$$a = -2\langle\varphi_{A1}|d_{1z}|\varphi_{A1}'\rangle\langle\varphi_{A2}'|d_{2z}|\varphi_{A2}\rangle, \tag{7}$$

and $\hat{T}$ is the kinetic-energy operator for the relative motion of the atoms.

In the case of exact resonance ($\epsilon_1 = \epsilon_2 = \epsilon$) the system (6) reduces to two independent equations for the functions $\psi^{(\pm)} = \psi_1 \pm \psi_2$:

$$[\hat{T} - (\varepsilon - U^{(\pm)})]\varphi^{(\pm)} = 0, \tag{8}$$

where $U^{(\pm)}(R) = \mp|a|/R^2$. The functions $\varphi^{(\pm)}$ describe states symmetric and antisymmetric under interchange of the atoms. Consequently, the problem of scattering in channels 1 and 2 effectively reduces to the problem of the elastic scattering of "quasibosons" and "quasifermions" in the respective fields $U^{(+)}(R)$ and $U^{(-)}(R)$.

The calculation of the trace of the operator $\exp\{-\hat{p}^2/mT\}$ by means of the eigenfunctions $\varphi^{(\pm)}$ leads to the following generalization of the well known Beth-Uhlenbeck formula[6] for the second virial coefficient:

$$B = -\frac{2\sqrt{2}}{\pi}\lambda^3\int_0^\infty dk\exp\left\{-\frac{\beta\hbar^2}{m}k^2\right\}\Big[\sum_l{}'(2l+1)\frac{\partial\delta_l^{(+)}(k)}{\partial k} + \sum_l{}''(2l+1)\frac{\partial\delta_l^{(-)}(k)}{\partial k}\Big], \tag{9}$$

where Σ' and Σ'' denote summations over even and odd l, respectively, $\delta_l^{(\pm)}(k)$ are the scattering phase shifts in the potentials $U^{(\pm)}$, $\lambda = (2\pi\hbar^2\beta/m)^{1/2}$, and $\beta \equiv 1/T$. Accordingly, to get the contribution of the interaction of the atoms in the continuous spectrum it is necessary to calculate the phase shifts $\delta_l^{(\pm)}(k)$.

3. Because of the large range of the interaction we can calculate $\delta_l^{(\pm)}(k)$ in the quasiclassical approximation:

$$\delta_l^{(\pm)} = \int_{r_0^{(\pm)}}^\infty \sqrt{k^2 - \frac{l^2}{r^2} - \frac{2mU^{(\pm)}}{\hbar^2}}\,dr - \int_{r_1}^\infty \sqrt{k^2 - \frac{l^2}{r^2}}\,dr. \tag{10}$$

Here $r_0^{(\pm)}$ and r_1 are the turning points of the classical motion in the fields $U^{(\pm)}$ and of the free motion, respectively. Using the traditional expansion of the integrand in (10) in powers of

$$\alpha \equiv \frac{2mU^{(\pm)}}{\hbar^2}\Big/\left(k^2 - \frac{l^2}{r^2}\right)$$

and also taking $r_0^{(\pm)} = r_1$ in first approximation, we get for the first-approximation phase shifts $\delta_l^{(\pm)(1)}$ the formula

$$\delta_l^{(\pm)(1)} = \pm l\gamma\int_1 \frac{dz}{z^3(1 - 1/z^2)^{1/2}} = \pm l\gamma, \tag{11}$$

where

$$\gamma = m|a|k/\hbar^2 l^3 \equiv l_0^3/l^3,$$

$z = kr/l$ is the dimensionless coordinate, and $z_1 = kr_1/l = 1$ is the dimensionless turning point in the free motion.

Since $\delta_l^{(+)(1)} = -\delta_l^{(-)(1)}$, the contribution to the second virial coefficient (9) from the phases $\delta_l^{(\pm)(1)}$ is determined by the derivative $\partial\delta_l^{(+)(1)}/\partial l$. Since $\delta_l^{(\pm)(2)} \gg \partial\delta_l^{(\pm)(1)}/\partial l$, it is necessary to calculate higher approximations for the phase shifts $\delta_l^{(\pm)}$. Simple estimates show that the higher-order approximations $\delta_l^{(\pm)(2)}$, $\delta_l^{(\pm)(3)}$, etc. make contributions of the same order of magnitude. Accordingly it is necessary to sum the whole infinite series of the expansion of $\delta_l^{(\pm)}$ in powers of α. Furthermore, in the calculations of higher approximations it is necessary to take into account the difference between the turning points $z_0^{(\pm)}$ and z_1. For this the expansion in the parameter α is not convenient.

We proceed in the following way. We put (10) in the form

$$\delta_l^{(\pm)} = l\int_C^\infty\left[\sqrt{1 - \frac{1}{z^2} \pm \frac{2\gamma}{z^3}} - \sqrt{1 - \frac{1}{z^2}}\right]dz + \Delta\delta_l^{(\pm)}, \tag{12}$$

where

$$\Delta\delta_l^{(\pm)} = l\int_{z_0^{(\pm)}}^C \sqrt{1 - \frac{1}{z^2} \pm \frac{2\gamma}{z^3}}\,dz - l\int_{z_1}^C \sqrt{1 - \frac{1}{z^2}}\,dz, \tag{13}$$

$z_0^{(\pm)} \approx 1 \pm \gamma$, $z_1 = 1$, and C is a limit not yet determined. Expanding the first square root in (12) in powers of $(1/z^2 \pm 2\gamma/z^3)$ and the second in powers of $1/z^2$, we get the following expression for $\delta_l^{(\pm)} - \Delta\delta_l^{(\pm)}$:

$$\delta_l^{(\pm)} - \Delta\delta_l^{(\pm)} = -l\int_C^\infty\sum_{n=1}^\infty\frac{(2n-1)!!}{(2n)!!(2n-1)}\sum_{p=1}^n\frac{n!}{p!(n-p)!} \times\left(\frac{1}{z^2}\right)^{n-p}\left(\mp\frac{2\gamma}{z^3}\right)^p dz \equiv \sum_{p=1}^\infty \delta_l^{(\pm)(p)}. \tag{14}$$

If we choose $C > 1$, this series converges uniformly in the entire range of integration and can be integrated term by term. Therefore it is convenient to choose $C = z_0^{(-)} > 1$. Integrating (14) term by term and also using the identity

$$\frac{p-n}{z_0^{(-)2n+p}} = \frac{1}{2}\,\frac{1}{z_0^{(-)3p-1}}\,\frac{d}{dz_0^{(-)}}$$

$$\left(z_0^{(-)3p-1}\frac{1}{z_0^{(-)2n+p-1}}\right) \equiv \hat{A}\left[\frac{1}{z_0^{(-)2n+p-1}}\right],$$

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[1] The expression (5) does not take into account transitions with change of the angular-momentum projections of the colliding atoms. The treatment given in [5] shows that inclusion of such transitions leads only to an unimportant change of the numerical coefficient in the final expression for the cross section. Therefore for simplicity we shall here use the wave function in the form (5).

we get for each term of the series in the sum over p:

$$\delta_l^{(\pm)(p+1)} = \frac{\pm 2\gamma}{p+1}\hat{A}\Big[l\frac{(\mp 2\gamma)^p}{p!}\sum_{n=p}\frac{(2n-1)!!}{(2n)!!(2n-1)!}\frac{n!}{(n-p)!}$$
$$\times\frac{1}{2n+p-1}\frac{1}{z_0^{(-)2n+p-1}}\Big(1-\frac{1}{2n+p}\Big)\Big]$$

We obviously make no great error if we neglect the term $1/(2n+p)$ in comparison with unity in the last parentheses. Then the expression in square brackets is equal to $\delta_l^{(\pm)(p)}$; that is, we have the recurrence relation

$$\delta_l^{(\pm)(p+1)}(z_0^{(-)}) \approx \frac{(\mp 2\gamma)}{p+1}\hat{A}[\delta_l^{(\pm)(p)}(z_0^{(-)})], \tag{15}$$

which allows us to express the correction in any order in terms of $\delta_l^{(\pm)(1)}$:

$$\delta_l^{(\pm)(p)} \approx \frac{(\mp 2\gamma)^{p-1}}{n!}\hat{A}^{p-1}[\delta_l^{(\pm)(1)}(z_0^{(-)})]. \tag{16}$$

To get the $\delta_l^{(\pm)(1)}(z_0^{(-)})$ themselves, there is no need to sum the series (14) over n for p = 1. It is readily seen that this series is the ordinary expansion in powers of α, with a further expansion in powers of $1/z^2$ made in each term, and with $C = z_0^{(-)}$ taken instead of the lower limit. Therefore it is easy to get the required expression for $\delta_l^{(\pm)(1)}(z_0^{(-)})$ from (11), by replacing unity as the lower limit by the quantity $z_0^{(-)}$:

$$\delta_l^{(\pm)(1)} = \pm l\gamma\int_{z_0^{(-)}}^{\infty}\frac{dz}{z^3(1-1/z^2)^{1/2}} = \pm l\gamma\Big(1-\sqrt{1-\frac{1}{z_0^{(-)2}}}\Big). \tag{17}$$

By means of (15), (16), and (17) we get up to terms $\sim 1/l_0 \ll 1$:

$$\delta_l^{(\pm)(p)} = \pm(\mp 1)^{p-1}\frac{\gamma^p}{p!}l\frac{(2p-3)!!}{(2p-3)}\frac{1}{z_0^{(-)p}(\sqrt{z_0^{(-)2}-1})^{2p-3}},$$
$$p = 2, 3, \ldots, \tag{18}$$

and use of the explicit expression for $z_0^{(-)}$ then gives

$$\delta_l^{(\pm)(p)} \approx \pm(\mp 1)^{p-1}(2\gamma)^{3/2}\frac{(2p-3)!!}{(2p)!!(2p-3)}l + O(\gamma^{5/2}); \quad p = 2, 3, \ldots. \tag{19}$$

To this same accuracy calculation of $\Delta\delta_l^{(\pm)}$ from (13) gives

$$\Delta\delta_l^{(+)} = \frac{7}{3\sqrt{2}}\gamma^{3/2}l, \quad \Delta\delta_l^{(-)} = -\frac{4+\sqrt{2}}{6}\gamma^{3/2}l.$$

When we carry out the sum over p in the expression

$$\delta_l^{(\pm)} = \delta_l^{(\pm)(1)} + \sum_{p=2}^{\infty}\delta_l^{(\pm)(p)} + \Delta\delta_l^{(\pm)}$$

we get the final result

$$\delta_l^{(-)} = -\frac{16-5\sqrt{2}}{6}\nu^{3/2}l - \gamma l, \qquad \delta_l^{(+)} = -\frac{1}{6\sqrt{2}}\gamma^{3/2}l + \gamma l. \tag{20}$$

We shall now use these expressions to calculate the second virial coefficient. In doing the sum over l in the integrand of (9) we must allow for the fact that the sum containing $\delta_l^{(+)}$ is taken over even l and that with $\delta_l^{(-)}$ over odd l:

$$\sum_{l_0}^{\infty}{}'(2l+1)\frac{\partial\delta_l^{(+)}}{\partial k} + \sum_{l_0}^{\infty}{}''(2l+1)\frac{\partial\delta_l^{(-)}}{\partial k}$$
$$= \sum_{p=l_0/2}^{\infty}(4p+1)\frac{\partial\delta_{2p}^{(+)}}{\partial k} + \sum_{p=l_0/2}^{\infty}(4p+3)\frac{\partial\delta_{2p+1}^{(-)}}{\partial k}.$$

In this expression the summation can be replaced with an integration between the limits $l_0/2$ and ∞:

$$\sum{}' + \sum{}'' \approx \int_{l_0/2}^{\infty}4p\frac{\partial\delta^{(+)}(2p)}{\partial k}dp + \int_{l_0/2}^{\infty}4p\frac{\partial\delta^{(-)}(2p+1)}{\partial k}dp$$
$$\approx -1.8\frac{l_0^3}{k} + 2\frac{l_0^2}{k}. \tag{21}$$

Substituting (21) in (9) and doing the integration over k, we get the following expression for the second virial coefficient:

$$B(T) \approx 7{,}2\pi\frac{|a|}{T} - 7\Gamma\Big(\frac{1}{3}\Big)\frac{\hbar|a|^{2/3}}{m^{1/2}T^{7/6}} \equiv B_1(T) + B_2(T), \tag{22}$$

$$\Gamma(x) = \int_0^{\infty}e^{-t}t^{x-1}\,dt.$$

In Eq. (22) the first term $B_1(T)$ is the main one and does not depend on the mass of the atoms. Since $B_1(T)$ is proportional to l_0^3 and the transport (diffusion) scattering cross section is proportional to l_0^2,[1] as we should expect, the change of pressure in the system when the external source is turned on shows the dependence $\Delta P \sim (\sigma_{tr}/r_0^2)^{3/2}$, where $r_0 = (4\pi n'/3)^{-1/3}$ is the mean distance between excited atoms, n′ being the density of these atoms.

The second term $B_2(T)$ in (22) arises because of the presence of the terms $\pm\gamma l$ in the expression for $\delta_l^{(\pm)}$; these terms appeared in the calculation of $\delta_l^{(\pm)(1)}$. In the sum over l in (9) each of these terms leads to a logarithmically diverging expression, which corresponds to the well known divergence of the second virial coefficient in a system of particles with an interaction inversely proportional to the cube of the distance between particles. There is no such divergence in the present problem, since because there are two scattering channels the $\delta_l^{(1)}$ occur in (9) in the combination

$$\delta_l^{(+)(1)} + \delta_{l-1}^{(-)(1)} \approx \delta_l^{(+)(1)} - \delta_{l-1}^{(+)(1)} \sim \partial\delta_l^{(1)}/\partial l.$$

Owing to this $B_2(T)/B_1(T) \sim 1/l_0 \ll 1$.

4. To estimate the size of the second virial coefficient it is convenient to express the value of |a| in terms of the probability of the dipole transition:

$$|a| \approx {}^3/_2 A\hbar c^3/\omega^3,$$

where ω is the frequency of the transition and A is the probability of the dipole transition (the Einstein coefficient). For allowed dipole transitions $A \sim 10^7-10^8\ \mathrm{sec}^{-1}$, and $\hbar\omega$ is a quantity of the order of several electron volts. Taking for our estimate $\hbar\omega \sim 3$ eV and $A = 10^8\ \mathrm{sec}^{-1}$, we have $|a| = 5 \times 10^{-35}\ \mathrm{g\ cm^5/sec^2}$.

Recalling that the fractional contribution to the pressure of the system corresponding to B(T) is

$$\Delta P/P = nn'B(T)/(n+n'),$$

we find that in the case $n \approx n' \sim 1.2 \times 10^{19}\ \mathrm{cm}^{-3}$ at normal temperature $\Delta P/P$ is 15 percent. Accordingly, at pressure 1 atm the gas is already essentially nonideal.

We can compare $B_1(T)$ with the corresponding quantity for an equivalent system of elastic spheres of diameter a_0. In order of magnitude $B_1(T)/a_0^3 \sim e^2/Ta_0 \sim 10^3$ (where e is the charge of the electron) at normal temperature. It is interesting that in this case the virial coefficients are in the ratio of the Coulomb scattering amplitude $f = e^2/T$ and the scattering amplitude for elastic spheres ($\sim a_0$).

We note that the heat capacity of our gas at constant volume is the same as that of an ideal gas if we use only the first term in (22). The quantity c_p, however, depends not only on the temperature but also on the volume and cannot be constant. In fact,

$$c_p - c_v = -T\left(\frac{\partial P}{\partial T}\right)_V^2 \Big/ \left(\frac{\partial P}{\partial V}\right)_T = R - 2R\frac{B_1(T)N'}{V},$$

where R is the gas constant.

In conclusion we note that this nonideality of the system can introduce corrections in the calculated characteristics of gas lasers, in particular in the value of the collision width of atomic levels.

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