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DISTRIBUTION OF CLUSTERS IN ALKALI METAL VAPOURS[1]

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Based on the laws of mass action between monomers and small neutral clusters (dimers, trimers, ...), the concentration of these clusters is calculated for dense alkali metal vapours as function of temperature and density. The laws of mass action are evaluated in simple approximations where the influence of interaction corrections to the ideal gas behaviour as well as the inclusion of internal degrees of freedom is studied. Explicit calculations are performed for dense cesium vapour. Solving the respective equation of state and investigating the stability behaviour, the gas-liquid phase transition is already described. The estimates for the critical point deviate from the respective experimental data. The present simple model has to be improved by considering also the ionization equilibrium and further interaction corrections to the thermodynamic functions.

1. Introduction

Precise measurements of the thermodynamic, electrical, and magnetic properties including the exact location of the critical point (e.g. for Cs: T_c=1924 K, p_c=92.5 bar, ρ_c=0.38 g/cm^3) are available for fluid alkali metals over the whole liquid-vapour coexistence range [1, 2]. The data clearly demonstrate that drastic changes of the electronic properties occur from phase to phase. While the liquid phase is highly conducting, the vapour phase is insulating far below the critical point. The distinctions between the coexisting phases vanish near to the liquid-vapour critical point and both phases show a non-metallic behaviour. For instance, the corresponding metal–non-metal transition for Cs is located at the critical point of the liquid-vapour phase transition.

It is generally accepted that the two limiting cases of the dense liquid metal and the low-density vapour phase are reasonably well understood. However, a theoretical description of the whole liquid-vapour coexistence curve has also to treat the electronic transition near the critical point. The connection between these limits through the critical point of the phase diagram has been performed within simplified models [3, 4].

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A unified treatment has to include both limiting cases, van der Waals and metallic bonding, and their interplay as function of density and temperature [5, 6].

Starting from the low-density vapour, atoms Cs are the elementary constituents for a statistical description. Distinct deviations from a strictly atomic behaviour have been observed for the compressibility [7] and the magnetic susceptibility [2] of dense cesium vapour. Estimates based on Saha equations for an ideal gas show that small neutral clusters such as dimers Cs_2 and trimers Cs_3 may occur in considerable concentrations [8]. It is the aim of the present paper to study the influence of non-ideality corrections to these Saha equations within simple models and to include the internal degrees of freedom (vibration, rotation) to the partition functions of these clusters. These corrections become more pronounced for the dense vapour region near the critical point.

2. Ideal Saha equations

The thermodynamic state of a system can be defined by means of the density of the free energy $f = F/V$, where F and V denote the free energy and the volume, respectively. For an ideal gas of particles having mass m, the density of the free energy is given by

$$f_{id} = nk_BT[\ln(n\lambda^3/Z) - 1], \tag{1}$$

where $\lambda^2 = 2\pi\hbar^2/(mk_BT)$ is the thermal wave length, and Z is the internal partition function. The equation for the chemical potential as function of the density and temperature,

$$\mu_{id} = k_BT\ln[n\lambda^3/Z], \tag{2}$$

is obtained from the relation $\mu = \delta f/\delta n$.

In thermodynamic equilibrium, the chemical potentials of the reacting species are equal. Neutral clusters can be described as bound states of atoms characterized by a binding energy E_j. Interaction corrections between monomers and clusters can be described by a pair potential $V_{ij}(r)$ via, e.g., virial coefficients.

We consider first the reaction between monomers (M) in the low-density vapour leading to the formation of dimers (D),

$$2Cs \rightleftharpoons Cs_2, \tag{3}$$

for which the chemical potentials fulfil the relation:

$$E_D + \mu_D = 2\mu_M. \tag{4}$$

E_D is the dissociation energy of dimers. The ideal law of mass action is then described by

$$\frac{n_D}{n_M^2} = \sqrt{8}\lambda_M^3 \exp(-\beta E_D). \tag{5}$$

Considering also further reactions such as the formation of trimers, we have to determine two reaction constants in the system simultaneously:

$$2Cs \rightleftharpoons Cs_2\ ,\ Cs_2 + Cs \rightleftharpoons Cs_3. \tag{6}$$

For the chemical potentials, we find the relations

$$2\mu_M = \mu_D + E_D\ ,\ \mu_D + \mu_M = \mu_T + E_T, \tag{7}$$

with the binding energies E_T and E_D. The respective law of mass action for the trimer reads now:

$$\frac{n_T}{n_M^3} = \sqrt{27}\lambda_M^6 \exp(-\beta(E_D + E_T)). \tag{8}$$

3. Internal degrees of freedom

The internal partition functions Z of the various constituents include, besides the spin and electronic degrees of freedom considered so far, also further contributions. For instance, molecules consisting of two atoms can be described by a dumbbell model, see Fig. 1. In addition, vibrational and rotational modes contribute to the partition function.

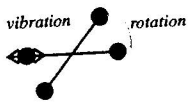

Fig. 1. Internal degrees of freedom for a dimer within the dumbbell model.

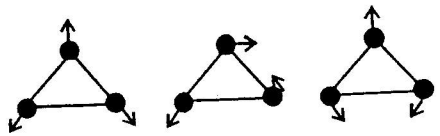

Fig. 2. Main vibration modes for a trimer.

Usually, the various internal degrees of freedom are separated. For the law of mass action for the dimers, Eq. (5), then follows:

$$\frac{n_D}{n_M^2} = \sqrt{8}\lambda_M^3 \exp(-\beta E_D)\sigma^{sp}\sigma^{rot}\sigma^{vib}. \tag{9}$$

The internal degrees of freedom can be expressed by [9]:

$$\sigma^{rot} = \beta hc/B_m, \tag{10}$$

where B_m is the characteristic rotational temperature, and

$$\sigma^{vib} = [1 - \exp(-\omega_m/\beta hc)]^{-1}, \tag{11}$$

where ω_m is the characteristic vibrational frequency of the cluster, h is Planck's constant, and c is the speed of light. σ^{sp} denotes the spin degree of freedom. For a dimer, we have $\sigma^{sp} = 1/2$, whereas for a trimer $\sigma^{sp} = 1$ follows.

For a trimer, a modified spectrum of internal degrees of freedom applies. Especially, three main modes for vibration with corresponding frequencies are found, see Fig. 2.

For the law of mass action for the trimer, Eq. (8), then follows:

$$\frac{n_T}{n_M^3} = \sqrt{27}\lambda_M^6 \exp\left(-\beta(E_D + E_T)\right) \sigma^{sp}\sigma^{rot} \prod_{i=1}^{3} \sigma_i^{vib} . \tag{12}$$

4. Interaction corrections

In a dense vapour, interaction corrections to the equation of state as well as to the mass action laws become of importance which can be treated by consistent (quantum) statistical methods [10]. In a simplified description, the density of the free energy of a system of neutral particles can be separated into an ideal and an interaction part, $f = f^{id} + f^{int}$. These non-ideality corrections can then be introduced formally via interaction parts of the chemical potentials and depend on the various partial densities in the system:

$$\mu_j = \mu_j^{id} + \triangle\mu_j \; , \; \triangle\mu_j = \triangle\mu_j(n_1 \ldots n_j) . \tag{13}$$

The partial density of dimers, Eq. (5), is then given by

$$\begin{aligned} n_D &= \frac{1}{\lambda_D^3}\sigma^{sp}\sigma^{vib}\sigma^{rot} \\ &\times \exp\left[\beta(2\mu_M^{id} - E_D + 2\triangle\mu_M(n_D, n_M) - \triangle\mu_D(n_D, n_M))\right] \; , \end{aligned} \tag{14}$$

and has to be calculated selfconsistently dependent on the total density and the temperature via:

$$\begin{aligned} F_0 &= \ln\left[\frac{n_D\lambda_D^3}{n_M^2\lambda_M^6}\right] + \beta E_D - \ln(\sigma^{sp}\sigma^{vib}\sigma^{rot}) \\ &+ \beta[\triangle\mu_D(n_D, n_M) - 2\triangle\mu_M(n_D, n_M)] = 0 . \end{aligned} \tag{15}$$

The interaction part of the density of the free energy for a system consisting of neutral particles can be split into the contributions [11],

$$f^{int} = f_{vdW} + f_{HC} , \tag{16}$$

where f_{vdw} describes the long-range attractive forces between neutrals (van der Waals corrections), whereas f_{HC} denotes the short-range repulsive forces due to the Pauli exclusion principle (hard core corrections). The van der Waals term f_{vdW} is calculated within a virial expansion,

$$f_{vdW} = n_i n_j k_B T B_{ij}(T) , \tag{17}$$

taking into account only the second virial coefficient:

$$B_{ij} = 2\pi \int_0^\infty \left[1 - \exp(-\beta V_{ij}(r))\right] r^2 dr . \tag{18}$$

For the calculation of the virial coefficients, we utilize the Sutherland-potential [9],

$$V^S(r) = \begin{cases} \infty & \text{if } r < \sigma \\ -C_6/r^6 & \text{if } r > \sigma \end{cases} . \tag{19}$$

Tab. 1. Parameters for the calculation of the laws of mass action, Eqs. (22) and (12), for dimers and trimers. E_j: binding energy, R: atomic radius, d: equilibrium distance in dimers, B_m: rotational temperature, ω_m: vibrational frequencies, C_6: van der Waals constant.

	atom	dimer	trimer
E_j (in eV)	-	-0.394	-0.352
R (in nm)	0.274	-	-
d (in nm)	-	0.461	-
B_m (in 1/cm)	-	0.0127	0.0125
ω_m (in 1/cm)	-	42.02	43.0, 20.0, 13.0
C_6 (in Ryd/a_B^6)	6800	-	-

The second virial coefficient is then given analytically by

$$B(T) = \frac{2\pi N\sigma^3}{3}\left[1 - \sum_{j=1}^{\infty} \frac{1}{j!}\frac{3}{j^3}\left(\frac{C_6}{\sigma^6 k_B T}\right)^j\right] . \tag{20}$$

The parameters for the Sutherland potential between Cs atoms are given in table 1, where σ is identified with the atomic radius R. The virial coefficients for the interaction between atoms and dimers B_{MD}, as well as between dimers B_{DD}, can be derived from that for the atoms, B_{MM}, via London's relation [9] which yields [12]:

$$B_{MD} = 0.45 B_{MM} \; , \; B_{DD} = 0.40 B_{MM} . \tag{21}$$

For the hard core term, analytic expressions are known for the case of a monoatomic fluid [13] as well as for mixtures [14]. We have utilized the latter expression and have, therefore, to determine the various hard core radii R_j. These data can be found again in table 1, where the effective hard core radii for the dimer (and, in principle, also for the trimer) can be calculated from the atomic radius and the equilibrium distances in these clusters. The detailed expressions for μ_{HC} are given elsewhere [15].

Making the different interaction corrections explicit, the following equation is derived from (15):

$$\begin{aligned} F_0 &= C + 2\left[n_D B_{DD}(T) - 2n_M B_{MM}(T)\right] \\ &+ B_{MD}(T)(n_M - 2n_D) + \beta\mu_D^{HC} - 2\mu_M^{HC} = 0 . \end{aligned} \tag{22}$$

5. Results and discussion

Within this simple model, we have calculated the equilibrium distribution of monomers, dimers, and trimers for fixed temperatures dependent on the total density for a dense, low-temperature cesium vapour. The respective parameters needed for the evaluation of Eqs. (22) and (12) are given in table 1.

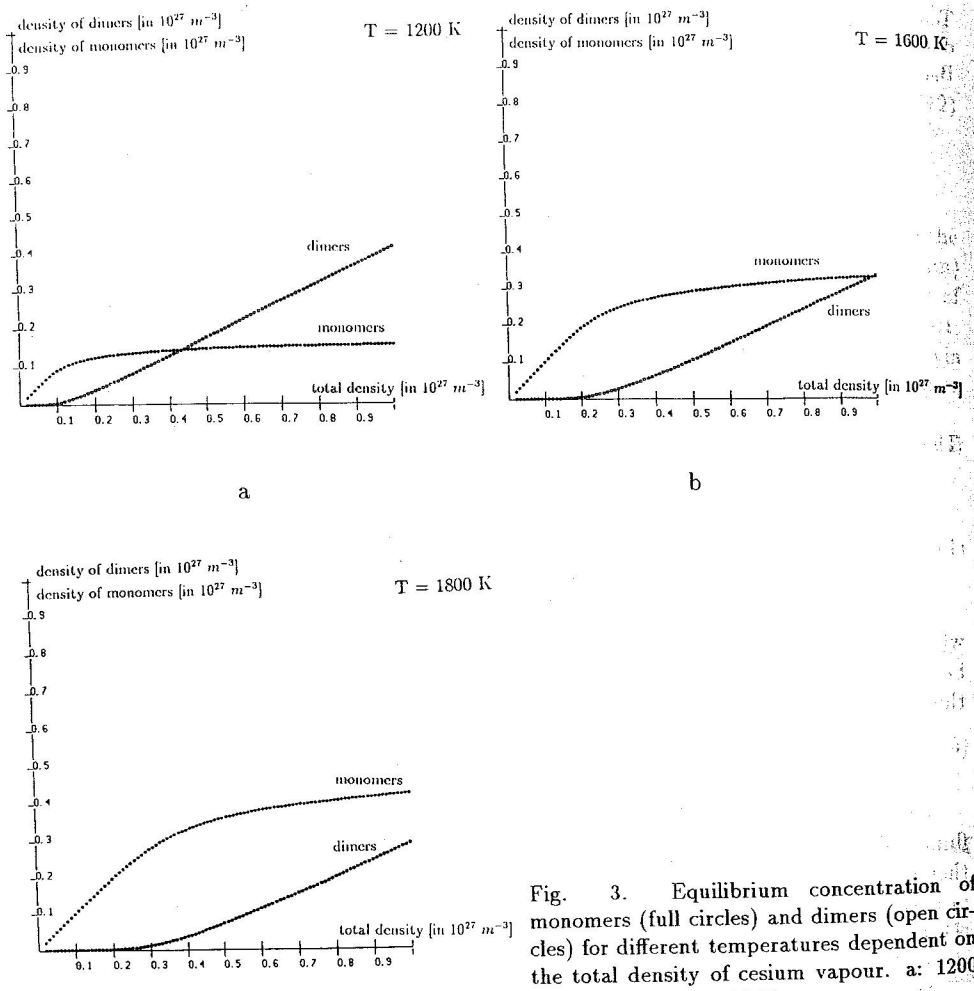

Fig. 3. Equilibrium concentration of monomers (full circles) and dimers (open circles) for different temperatures dependent on the total density of cesium vapour. a: 1200 K, b: 1600 K, c: 1800 K.

The results for the composition are shown in Fig. 3 for densities up to 10^{27} particles per m^3. The number of dimers increases with density. For higher temperatures, the concentration of dimers becomes less pronounced. The concentration of trimers can be neglected within this simple approach contrary to earlier results in [8]. At higher densities, non-ideality corrections cause a slightly non-linear behaviour.

Near to the experimetally determined critical isotherm (Fig. 3c), the dimer concentration amounts about 25%. From the measurements of the magnetic susceptibility [2], a dimer concentration of about 20% can be deduced. This ratio has been confirmed recently within a quantum statistical calculation for the equation of state and the magnetic susceptibility [12].

The effect of including the internal degrees of freedom for the dimer and trimer is considerable when calculating their equilibrium concentrations. Neglecting the vibrational and rotational modes, the concentration of dimers and trimers is too small by a factor of about 10^4 and 10^5, respectively, and the vapour would be purely atomic.

The model system considered here shows already a thermodynamic instability. The region of this phase transition can be extracted from the stability criterion for the chemical potential, $\delta\mu/\delta n \geq 0$. As a special characteristic of the phase diagram, the critical point of this vapour-liquid phase transition is located at a critical temperature of T_c=780 K and a critical density of n_c=8.3 $\times$ 10^{27} m^{-3}. There, a concentration of 82% dimers and 18% monomers follows within our model.

In order to give an estimate for the influence of clusters, we compare these results with those for the pure systems of only monomers or dimers. We obtain the values T_c=5950 K for the system of monomers, and T_c=605 K for the system of dimers. The calculated value for the critical temperature lies between the data for the pure systems as expected. The result for the pure atomic system lies far above the measured value for the critical temperature, whereas the result for the pure molecular system is too small. However, this value coincides with a result of T_c=826 K for molecular J_2 which was obtained from a simple van der Waals equation of state which takes into account hard sphere correction terms [16].

Taking into account a more realistic potential for the $Cs_2 - Cs_2$ interaction, the theoretical result for the critical temperature is in better agreement with the measured value, T_c=2325 K [17]. Furthermore, excited states of the cesium dimers are predicted which are not included in our simple model.

The critical temperature of the gas-liquid phase transition within the present simple model of a neutral gas consisting of only monomers, dimers, and trimers is too small compared with the experimental value of 1925 K [1]. The inclusion of the ionization equilibrium, i.e. the possibility of excitation of internal degrees of freedom, and the subsequent treatment of non-ideality corrections due to charges yields a better agreement with the experimental values as shown for the alkali-atom metals [5] as well as for mercury [18].

The critical pressures and densities are strongly affected by a variation of the hard core radii. Therefore, these parameters have to be derived from a more general microscopic treatment of the short-range interaction between atoms as given, for instance, in [19].

References

[1] F. Hensel, H. Stolz, G. Hohl, R. Winter, W. Götzlaff: J. de Phys. IV (Paris) Colloq. C5 (1991) 191
[2] W. Freyland: Phys. Rev. B 20 (1979) 5104
[3] V.A. Alekseev, I.T. Iakubov: Phys. Rep. 96 (1983) 1
[4] J.P. Hernandez: Phys. Rev. Lett. 53 (1984) 2320; Phys. Rev. A 31 (1985) 932
[5] R. Redmer, G. Röpke: Contrib. Plasma Phys. 29 (1989) 343
[6] E. Chacón, J.P. Hernandez, P. Tarazona: J. Phys.: Condens. Matter 5 (1993) 1753

[7] C.T. Ewing, J.P. Stone, J.R. Spann, R.R. Miller: J. Phys. Chem. 71 (1967) 473
[8] N.N. Iermohin, B.M. Kovaliov, P.P. Kulik, V.A. Riabii: J. de Phys. (Paris) Colloq. 39 (1978) C1-200
[9] J.D. Hirschfelder, C.F. Curtiss, R.B. Bird: *Molecular Theory of Gases and Liquids* (Wiley, New York, 1954)
[10] W.-D. Kraeft, D. Kremp, W. Ebeling, G. Röpke: *Quantum Statistics of Charged Particle Systems* (Akademie-Verlag, Berlin, 1986)
[11] W. Ebeling, W.-D. Kraeft, D. Kremp: *Theory of Bound States and Ionization Equilibrium in Plasmas and Solids* (Akademie-Verlag, Berlin, 1976)
[12] R. Redmer, W.W. Warren, Jr.: Phys. Rev. B 48 (1993) 14892
[13] N.F. Carnahan, K.E. Starling: J. Chem. Phys. 51 (1969) 632
[14] G.A. Mansoori, N.F. Carnahan, K.E. Starling, T.W. Leland: J. Chem. Phys. 54 (1971) 1523
[15] W. Ebeling, K. Scherwinski: Z. Phys. Chem. (Leipzig) 264 (1983) 1
[16] D.A. Young, B.J. Alder: Phys. Rev. A 3 (1971) 364
[17] M. Ross, L. Yang, B. Dahling, N. Winter: Z. Phys. Chem. (1994)
[18] S. Nagel, G. Röpke, R. Redmer, F. Hensel: J. Phys.: Condens. Matter 6 (1994) 2137
[19] S. Nagel, H. Stein, I. Leike, R. Redmer, G. Röpke: J. Phys. B: At. Mol. Opt. Phys. 25 (1992) 613