

Binary Mixtures of Chiral Gases

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Abstract— A possible solution of the well known paradox of chiral molecules is based on the idea of spontaneous symmetry breaking. At low pressure the molecules are delocalized between the two minima of a given molecular potential while at higher pressure they become localized in one minimum due to the intermolecular dipole-dipole interactions. Evidence for such a phase transition is provided by measurements of the inversion spectrum of ammonia and deuterated ammonia at different pressures. In particular, at pressure greater than a critical value no inversion line is observed. These data are well accounted for by a model previously developed and recently extended to mixtures. In the present paper, we discuss the variation of the critical pressure in binary mixtures as a function of the fractions of the constituents.

1. INTRODUCTION

According to quantum mechanics chiral molecules, that is, molecules which are not superimposable on their mirror image, should not exist as stable stationary states. Consider ammonia NH_3 . The two possible positions of the N atom with respect to the plane of the H atoms are separated by a potential barrier and can be connected via tunneling. This gives rise to stationary wave functions delocalized over the two minima of the potential and of definite parity. In particular, the ground state is expected to be even under parity. Tunneling induces a doublet structure of the energy levels.

On the other hand, the existence of chiral molecules can be interpreted as a phase transition. In fact, isolated molecules do not exist in nature and the effect of the environing molecules must be taken into account to explain phenomena characterized by instabilities. This interpretation underlies a simple mean-field model developed in [1] to describe the transition of a gas of NH_3 molecules from a nonpolar phase to a polar one through a localization phenomenon which gives rise to the appearance of an electric dipole moment. Even if ammonia molecules are only pre-chiral [2], the mechanism, as emphasized in [1], provides the key to understand the origin of chirality.

A quantitative discussion of the collective effects induced by coupling a molecule to the environment constituted by the other molecules of the gas was made in [3]. In this work it was shown that, due to the instability of tunneling under weak perturbations, the order of magnitude of the molecular dipole-dipole interaction may account for localized ground states. This suggested that a transition to localized states should happen when the interaction among the molecules is increased.

Evidence for such a transition was provided by measurements of the dependence of the doublet frequency under increasing pressure: the frequency vanishes for a critical pressure P_{cr} different for NH_3 and ND_3 . The measurements were taken at the end of the 1940s and beginning of the 1950s [4–6] but, as far as we know, no quantitative universally accepted theoretical explanation exists in spite of many attempts. The model [1] gives a satisfactory account of the empirical results. A remarkable feature of the model is that there are no free parameters. In particular, it describes quantitatively the shift to zero-frequency of the inversion line of NH_3 and ND_3 on increasing the pressure.

Recently, we extended the model [1] to gas mixtures [7]. This case may be of interest, among other things, for the interpretation of the astronomical data such as those from Galileo spacecraft [8] which measured the absorption spectrum of NH_3 in the Jovian atmosphere. Formulas for the critical pressure of a general mixture have been provided.

In the present paper, we investigate the behavior of the critical pressure in binary mixtures. We show that the critical pressure of a chiral species can be increased or decreased by several orders of magnitude by mixing it with a proper fraction of a proper species, chiral or non polar.

2. CHIRAL GAS

We model a gas of all equal chiral molecules as a set of two-level quantum systems, that mimic the inversion degree of freedom of an isolated molecule, mutually interacting via the dipole-dipole

electric force. At moderate density, we approximate the behavior of the $N \gg 1$ molecules of the gas with the mean-field Hamiltonian

$$h(\psi) = -\frac{\Delta E}{2}\sigma^x - G\frac{\langle\psi, \sigma^z \psi\rangle}{N}\sigma^z, \quad (1)$$

where σ^x and σ^z are the Pauli matrices and ψ is the Pauli spinor representing the mean-field molecular state with normalization $\langle\psi, \psi\rangle = N$. The scalar product between two Pauli spinors is defined in terms of their two components in the standard way. The parameter ΔE is the inversion energy-splitting measured by spectroscopic methods in the rarefied gas. The parameter G accounts for the effective dipole interaction energy of a single molecule with the rest of the gas. It can be estimated in two different but equivalent ways [7].

The first way to estimate G is based on the so called Keesom energy, namely, G is identified with the effective dipole-dipole interaction obtained after averaging over all possible molecular distances and all possible dipole orientations. These averages are calculated assuming that, concerning the translational, vibrational, and rotational degrees of freedom, the N molecules behave as an ideal gas at thermal equilibrium at temperature T . This assumption relies on a sharp separation (decoupling) between these degrees of freedom and the inversion motion. The result is

$$G = \frac{4\pi}{9} \frac{\mu^4 P}{(4\pi\epsilon_0 k_B T)^2 d^3}, \quad (2)$$

where P is the pressure of the gas, μ the electric-dipole moment of the molecules and d the minimal distance between two molecules, namely, the so called molecular collision diameter. At fixed temperature, the effective interaction constant G increases linearly with the gas pressure P .

The second way to estimate G is based on the reaction field mechanism [9]. Let us consider a spherical cavity of radius a in a homogeneous dielectric medium characterized by a relative dielectric constant ϵ_r . An electric dipole $\boldsymbol{\mu}$ placed at the center of the cavity polarizes the dielectric medium inducing inside the sphere a reaction field \mathbf{R} proportional to $\boldsymbol{\mu}$. As a result, the dipole acquires an energy

$$\mathcal{E} = -\frac{1}{2}\boldsymbol{\mu} \cdot \mathbf{R} = -\frac{\epsilon_r - 1}{2\epsilon_r + 1} \frac{\mu^2}{4\pi\epsilon_0 a^3}. \quad (3)$$

Since $\epsilon_r \simeq 1$, we can approximate the first fraction in Eq. (3) by the Clausius-Mossotti relation

$$\frac{\epsilon_r - 1}{\epsilon_r + 2} = \frac{1}{3}\rho(\alpha + \alpha^D), \quad (4)$$

where α is the molecular polarizability and $\alpha^D = \mu^2/(3\epsilon_0 k_B T)$ is the Debye (orientation) polarizability. Observing that for a chiral gas $\alpha^D \gg \alpha$ (for instance, in the case of NH_3 we have $\alpha \simeq 2 \text{ \AA}^3$ whereas $\alpha^D \simeq 217 \text{ \AA}^3$ at $T = 300 \text{ K}$), we get

$$\mathcal{E} = -\frac{4\pi}{9} \frac{\mu^4 P}{(4\pi\epsilon_0 k_B T)^2 a^3}. \quad (5)$$

Microscopic arguments [10, 11] show that the radius of the spherical cavity a is not arbitrary but must be identified with the the minimum distance between two interacting molecules, namely, the molecular collision diameter d introduced in Eq. (2). We thus have $\mathcal{E} = -G$.

The state ψ collectively describing the inversion degree of freedom of the gas of N chiral molecules is determined as the minimal-energy stationary state of the Hamiltonian of Eq. (1). This corresponds to find the lowest-energy eigenstate of the nonlinear eigenvalue problem $h(\psi)\psi = \lambda\psi$, with the constraint $\langle\psi, \psi\rangle = N$. We refer the reader to [1, 7] for the mathematical details, here we just state the main results.

There exists a critical value of the interaction strength, $G_{\text{cr}} = \Delta E/2$, such that for $G < G_{\text{cr}}$ the mean-field eigenstate with minimal energy is $\psi = \sqrt{N}\varphi_+$, where φ_+ is the eigenstate of σ^x with eigenvalue $+1$, i.e., the molecules are delocalized. For $G > G_{\text{cr}}$ there are two degenerate solutions of minimal energy which can be termed chiral states, in the sense they are transformed into each other by the parity operator σ^x . For $G \gg G_{\text{cr}}$, these solutions become the localized states

$\sqrt{N}\varphi_L, \sqrt{N}\varphi_R$, where φ_L, φ_R are the eigenstates of σ^z . The energy associated with the state ψ is a continuous function of G with a discontinuous derivative at $G = G_{\text{cr}}$. We thus have a quantum phase transition between a delocalized (or achiral, or nonpolar) phase and a localized (or chiral, or polar) phase. In view of the dependence of G on P , we can define a critical pressure at which the phase transition takes place

$$P_{\text{cr}} = \frac{9}{8\pi} \frac{\Delta E d^3 (4\pi\epsilon_0 k_B T)^2}{\mu^4}. \quad (6)$$

Note that the value of P_{cr} is completely determined in terms of the microscopic parameters ΔE , μ and d and the temperature T .

In [1] we have also shown that in the delocalized phase the inversion angular frequency of the interacting molecules depends on the pressure as $\hbar\bar{\omega}(P) = \Delta E \sqrt{1 - P/P_{\text{cr}}}$. This formula is interesting as it expresses the ratio of two microscopic quantities, $\hbar\bar{\omega}$ and ΔE , as a universal function of the ratio of the macroscopic variables P and P_{cr} . Furthermore, it is in very good agreement with some spectroscopic data showing the shift to zero frequency of the inversion line of NH_3 or ND_3 at increasing pressures [4–6].

3. BINARY MIXTURES

Consider a gas mixture of two species labeled 1 and 2. In this case, the Clausius-Mossotti relation reads as

$$\frac{\epsilon_r - 1}{\epsilon_r + 2} = \frac{1}{3} (\rho_1 (\alpha_1 + \alpha_1^{\text{D}}) + \rho_2 (\alpha_2 + \alpha_2^{\text{D}})), \quad (7)$$

where the Debye polarization $\alpha_i^{\text{D}} = \mu_i^2 / (3\epsilon_0 k_B T)$ is given in terms of the molecular electric-dipole moment μ_i of the species $i = 1, 2$. According to the reaction field arguments discussed above, a chiral molecule, let us say of species i , having dipole moment μ_i , acquires, due to the interaction with all the other molecules of the mixture, the energy

$$\mathcal{E}_i = -\frac{1}{3} (\rho_1 (\alpha_1 + \alpha_1^{\text{D}}) + \rho_2 (\alpha_2 + \alpha_2^{\text{D}})) \frac{\mu_i^2}{4\pi\epsilon_0 d_i^3}, \quad (8)$$

where d_i is the molecular collision diameter of the i -th species. We now specialize the discussion in the following two cases.

3.1. Mixtures of a Chiral Gas with a Non Polar Gas

For a mixture of chiral and non polar molecules, the mean-field molecular state of the chiral species, assumed as species 1, is determined similarly to the case of a single chiral gas. The only degree of freedom of the non polar molecules is the deformation which, in turn, is proportional to the electric dipole moment of the chiral molecules. We may thus describe the mixture by a single mean-field molecular state, ψ_1 , normalized to the number of molecules of the species 1, $\langle \psi_1, \psi_1 \rangle = N_1$. As before, we assume that this state is determined as the lowest-energy eigenstate of the eigenvalue problem associated with the mean-field Hamiltonian

$$h_1(\psi_1) = -\frac{\Delta E_1}{2} \sigma_1^x - G_1 \frac{\langle \psi_1, \sigma_1^z \psi_1 \rangle}{N_1} \sigma_1^z. \quad (9)$$

In this Hamiltonian $-G_1$ represents the effective dipole interaction energy of a single chiral molecule with all the other molecules, chiral and non polar, of the mixture. Thus we can identify $-G_1 = \mathcal{E}_1$, where \mathcal{E}_1 is given by Eq. (8) with $i = 1$, $\alpha_1 \ll \alpha_1^{\text{D}}$, and $\alpha_2^{\text{D}} = 0$, namely,

$$G_1 = (\gamma_{11} P_1 + \gamma_{12} P_2), \quad (10)$$

$$\gamma_{11} = \frac{4\pi}{9} \frac{\mu_1^4}{(4\pi\epsilon_0 k_B T)^2 d_1^3}, \quad \gamma_{12} = \frac{1}{3} \frac{\alpha_2 \mu_1^2}{4\pi\epsilon_0 k_B T d_1^3}. \quad (11)$$

As usual we used the ideal gas relations $\rho_1 = P_1/k_B T$ and $\rho_2 = P_2/k_B T$, where P_1 and P_2 are the partial pressures of the two species.

The analysis of the nonlinear eigenvalue problem $h(\psi_1)\psi_1 = \lambda_1\psi_1$, with the constraint $\langle \psi_1, \psi_1 \rangle = N_1$, is identical to the case of a single chiral gas. We have a localization phase transition when

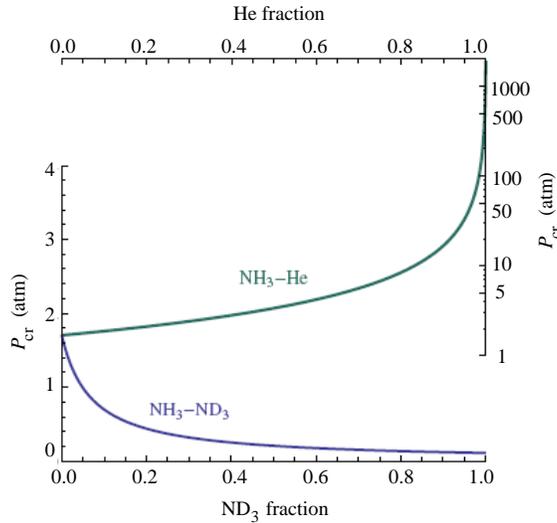


Figure 1: Critical pressure of the localization phase transition in a binary mixture of NH_3 as a function of the fraction of the second constituent chosen as ND_3 (bottom-left axes) or He (top-right axes).

$G_1 = \Delta E_1/2$. The transition can be considered as a function of the total pressure $P = P_1 + P_2$ of the mixture and of the fractions of the two species $x_1 = P_1/P$ and $x_2 = P_2/P$. In this case, instead of a unique critical pressure, we have a critical line parametrized by x_1 or $x_2 = 1 - x_1$, e.g.,

$$P_{\text{cr}} = \frac{\Delta E_1}{2x_1\gamma_{11} + 2x_2\gamma_{12}}. \quad (12)$$

In Fig. 1, we show the variation of the critical pressure in a NH_3 -He mixture as a function of the He fraction. The value of P_{cr} increases from the critical pressure of pure NH_3 to a maximum reached for a vanishing NH_3 fraction. The value of this maximum depends on the nature of the non polar species, it is greater the smaller is the molecular polarizability α_2 .

3.2. Mixtures of Two Chiral Gases

For a mixture of two chiral gases, we describe the inversion degrees of freedom of the two species by mean-field molecular states ψ_1, ψ_2 normalized to the number of molecules of the corresponding species. These states are obtained as the lowest-energy eigenstates of the eigenvalue problem associated with the coupled mean-field Hamiltonians

$$h_1(\psi_1, \psi_2) = -\frac{\Delta E_1}{2}\sigma_1^x - \sum_{j=1}^2 G_{1j} \frac{\langle \psi_j, \sigma_j^z \psi_j \rangle}{N_j} \sigma_1^z, \quad (13a)$$

$$h_2(\psi_1, \psi_2) = -\frac{\Delta E_2}{2}\sigma_2^x - \sum_{j=1}^2 G_{2j} \frac{\langle \psi_j, \sigma_j^z \psi_j \rangle}{N_j} \sigma_2^z. \quad (13b)$$

Pauli operators now have a label $i = 1, 2$ relative to the species they refer to. Each term $-G_{ij}$ represents the effective dipole interaction energy of a single molecule of species i with all the other molecules of species j . By matching $-G_{i1} - G_{i2} = \mathcal{E}_i$, where \mathcal{E}_i is given by Eq. (8) with $\alpha_1 \ll \alpha_1^{\text{D}}$ and $\alpha_2 \ll \alpha_2^{\text{D}}$, we get

$$G_{ij} = \gamma_{ij}x_jP, \quad \gamma_{ij} = \frac{4\pi}{9} \frac{\mu_i^2 \mu_j^2}{(4\pi\epsilon_0 k_B T)^2 d_i^3}, \quad (14)$$

where P is the total pressure of the mixture and x_1, x_2 the fractions of the components.

The solution of the coupled nonlinear eigenvalue problem $h_1(\psi_1\psi_2)\psi_1 = \lambda_1\psi_1$ and $h_2(\psi_1\psi_2)\psi_2 = \lambda_2\psi_2$, with the constraints $\langle \psi_1, \psi_1 \rangle = N_1$ and $\langle \psi_2, \psi_2 \rangle = N_2$, is discussed in [7]. As in the case of a single chiral gas, the mixture undergoes a localization phase transition at a critical pressure P_{cr} . For $0 < P < P_{\text{cr}}$, the lowest-energy molecular state of the mixture corresponds to molecules of

both species in a delocalized symmetric configuration. For $P > P_{\text{cr}}$, new minimal-energy molecular states appear with twofold degeneracy. These states correspond to molecules of both species in a chiral configuration of type L or R . We have a particularly simple formula for P_{cr} ,

$$\frac{1}{P_{\text{cr}}} = \sum_{i=1}^2 x_i \frac{1}{P_{\text{cr}}^{(i)}}, \quad P_{\text{cr}}^{(i)} = \frac{\Delta E_i}{2\gamma_{ii}} = \frac{9}{8\pi} \frac{\Delta E_i d_i^3 (4\pi\epsilon_0 k_B T)^2}{\mu_i^4}, \quad (15)$$

the inverse critical pressure of the mixture is the fraction-weighted average of the inverse critical pressures of its components. In Fig. 1, we show the variation of the critical pressure in a NH_3 - ND_3 mixture as a function of the ND_3 fraction. The value of P_{cr} ranges from the critical pressure of pure NH_3 to that of pure ND_3 , namely, from 1.69 atm to 0.11 atm. By changing ND_3 with, for instance, D_2S_2 , the minimal value of P_{cr} can be extended down to 4.3×10^{-9} atm, the critical pressure of deuterated disulfane.

4. CONCLUSION

Our approach to the existence of chiral molecules is based on ideas of equilibrium statistical mechanics. One may be surprised by the presence of a quantum phase transition at room temperatures. We emphasize that the transition takes place only in the inversion degrees of freedom. The dynamics of these degrees of freedom is affected by temperature only through the values of the coupling constants.

We have shown that with the addition of a proper fraction of a second species, non polar or chiral, the critical pressure of an ammonia mixture can vary in a range of several orders of magnitude. As a consequence, the inversion line of ammonia, as well as, possibly, that of the second chiral constituent, should undergo a frequency shift rather different from that measured for pure gases, see [7]. An experimental verification of these predictions is well within the reach of present technology and would represent a critical test of our theory.

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