Nucleation phenomena
in a nonuniform atomic fluid
in the electrical field

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Abstract

The density functional approach is used to study the gas–to–liquid and liquid–to–gas nucleation phenomena in a fluid of two–level atoms in an external electrical field. The influence of the field on the surface tension and nucleation and cavitation barriers is discussed.

Key words: gas–liquid phase transition, density functional approach, density profile, surface tension, nucleation barrier, cavitation barrier

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In recent years a significant progress has been made in the molecular theory of the gas–to–liquid and liquid–to–gas phase transitions. An important contribution in this field is that of D. W. Oxtoby with coworkers\textsuperscript{1} who showed how the experimentally measured quantity, the nucleation rate, can be calculated starting from the interparticle interactions with the help of the density functional approach. The elaborated method seems to be valuable near the spinodal curve since it predicts a vanishing of the nucleation barriers (as it should be expected) in contrast to the well known classical nucleation theory which yields a finite value for the nucleation barriers. The results for the nucleation rate obtained within the framework of those theories differ near the binodal curve as well, however, a prediction of the classical nucleation theory in that case seems to be preferable. Both theories can be viewed as microscopic ones which are based on the density functional approach study of the planar interface (classical nucleation theory) or the spherical interface (nonclassical nucleation theory).

In the present paper we are following the influence of an external electrical field on the gas–to–liquid and liquid–to–gas nucleation phenomena. First we examine the
changes in the interparticle interactions due to the field adopting for this purpose a simple model of two–level atoms. After deriving the equation of state we make a guess about the form of the grand thermodynamic potential density functional, which takes into account the external electrical field. Finally, we performed standard density functional theory calculations to obtain the surface tension and nucleation barriers and discuss the influence of the external electrical field on these quantities.

To study the effective (long–range) interparticle interaction in the presence of the external electrical field we introduce two–level atoms with the excitation energy $E_1 - E_0$ and the value of the dipole transition moment $|\mathbf{p}|$. Using the quantum mechanical perturbation theory one immediately finds the long–range interparticle interaction between two atoms being at the distance $R_{12}$

$$ - \left( \frac{\alpha_{12}^2}{2} + \frac{\gamma_1^2 + \gamma_2^2}{4} \left( 1 + \frac{3\alpha_{12}^2}{2} \right) - \gamma_1 \gamma_2 \alpha_{12} \right) (E_1 - E_0) + \ldots . \quad (1) $$

Here

$$ \alpha_{ij}(E_1 - E_0) = \frac{|\mathbf{p}|^2}{R_{ij}^3} \Phi_{ij}, \quad \gamma_i(E_1 - E_0) = -2|\mathbf{p}||\mathbf{E}| \chi_i, \quad (2) $$

and $\Phi_{ij}$ and $\chi_i$ are the known in the theory of dipole systems orientational functions depending on the orientations of dipole transition moments. The first term in (1) is the usual van der Waals interaction, all other terms depend on the strength of the electrical field $|\mathbf{E}|$. We do not discuss a change in the short–range interaction due to the field taking it into account by means of the “atomic radius” $\sigma$.

We calculate further the equation of state repeating a text–book derivation of the second virial coefficient for the case when the long–range interaction between two hard–sphere–like particles is given by Eq. (1). The only peculiarity is the additional average over the orientations of dipole transition moments which we perform by means of the cumulant expansion. Although the calculations are rather tedious the final result for the virial state equation is simple [4]

$$ \frac{p}{kT} = \rho + \rho^2 B_2 + \ldots , \quad (3) $$

$$ B_2 = 4v - 2\pi \sigma^3 \int_{2\sigma}^\infty d\rho \rho^2 \left( \exp \left( \frac{N^2}{3\tau} \left( 1 + 2N^2 \mathcal{E}^2 \right) \frac{1}{\rho^6} \right) - 1 \right) , $$

where $v = \frac{4}{3} \pi \sigma^3$ and $\tau = \frac{kT}{E_1 - E_0}$ and $\mathcal{E} = \frac{|\mathbf{E}| \sigma^3}{|\mathbf{p}|}$ are the dimensionless temperature and the dimensionless strength of the electrical field, respectively. Within the adopted approximations the particle is characterized only by the dimensionless parameter $N = \frac{|\mathbf{p}|^2}{\sigma^3(E_1 - E_0)}$. In further computation we put for simplicity $N = 1$. As can be seen from Eq. (3) the only result of the external electrical field is the increasing of the van der Waals constant by $1 + 2N^2 \mathcal{E}^2$.

It is easy to construct the grand thermodynamic potential density functional [5] which yields for the uniform fluid of small density the virial state equation (3).
Thus, we shall examine the atomic fluid in the external electrical field on the basis of the following grand thermodynamic potential density functional

\[
\Omega[\rho(R)] = kT \int dR_1 \rho(R_1) \left( \ln \left( \Lambda^3 \rho(R_1) \right) + \frac{-1 + 6v\rho(R_1) - 4v^2\rho^2(R_1)}{(1 - v\rho(R_1))^2} \right)
- \frac{6\sigma^3a}{\pi} \int_{|R_1 - R_2| \geq 2\sigma} dR_1 dR_2 \frac{\rho(R_1)\rho(R_2)}{|R_1 - R_2|^6} - \mu \int dR_1 \rho(R_1), \tag{4}
\]

where \(\Lambda\) is the thermal wavelength, and the constant

\[
a = \frac{1}{48} v(E_1 - E_0) \zeta^2 (1 + 2\zeta^2\xi^2), \tag{5}
\]

Figure 1: Isotherms \(\pi = \pi \left( \frac{1}{\eta} \right)\) \((\pi = \frac{\rho v}{E_1 - E_0} \text{ and } \eta = \rho v \text{ are the dimensionless pressure and density, respectively})\) at \(\tau = 0.9\tau_c(\xi)\) (solid curves), binodal curves (long–dashed curves) and spinodal curves (short–dashed curves) in the absence of electrical field \((1, 3, 5)\) and in the presence of electrical field \(\xi = 0.5\) \((2, 4, 6)\).

which controls the contribution of the long–range interaction to \(\Omega[\rho(R)]\), depends on the strength of the field. The grand thermodynamic potential density functional \((4)\) takes into account the short–range interaction within the (local) Carnahan–Starling approximation and the long–range interaction within the (nonlocal) mean–field approximation. We also consider a simplified version of \((4)\) treating the long–range contribution within the local gradient approximation which is expected to yield a reasonable result for the temperatures only slightly lower than the critical temperature.
We proceed by applying to (4) the standard machinery of the density functional theory \[3\] (see also \[4, 5\]) seeking for a solution of the equation for density \(\frac{\delta\Omega[\rho(r)]}{\delta\rho(r)} = 0\) and evaluating the grand thermodynamic potential \(\Omega\). We examine the uniform fluid establishing the gas–liquid phase diagram and the nonuniform fluid with planar and spherical interface calculating the surface tension and the nucleation barriers for the saturated vapour and the tensile liquid. Our findings are collected in Figures 1–4.

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**Figure 2:** Temperature dependence of the surface tension \(\gamma\). In the left panel the dependence \(\gamma(\tau)\) for \(E = 0\) and \(E = 0.5\) is shown. In the right panel the result of the nonlocal treatment (solid curve) is compared with the one obtained within the gradient approximation (dotted curve).

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**Figure 3:** Gas–to–liquid nucleation barrier \(\frac{\alpha(\tau,s)}{\tau}\) vs. \(s\) or vs. \(\frac{1}{\eta}\) at \(\tau = 0.6\tau_c(E)\). Solid and dotted (gradient approximation) curves are obtained within the density functional approach. Dashed curves are obtained within the classical nucleation theory.
Let us discuss the obtained results. The phase diagram of the considered fluid is shown in Figure 1. The critical parameters are

\[ \rho_c v = \eta_c \approx 0.13044, \]
\[ \tau_c(\mathcal{E}) \approx 0.00196518N^2(1 + 2N^2 \mathcal{E}^2), \]
\[ \frac{p_c(\mathcal{E})v}{E_1 - E_0} = \pi_c(\mathcal{E}) \approx 0.00009202N^2(1 + 2N^2 \mathcal{E}^2). \]  

The electric field increases the critical temperature and pressure as can be expected. From the temperature dependence of the surface tension shown in the left panel in Figure 2 one concludes that it increases with switching on the field. However, this change is conditioned only by the increase of the critical temperature (6) and the dependence \( \gamma \) vs. \( \frac{T}{T_c(\mathcal{E})} \) (as in the right panel in Figure 2) is field independent. The nucleation barriers \( A \) calculated within the frames of the density functional theory (exploiting the nonlocal grand thermodynamic potential density functional or using the gradient approximation) as well as within the classical nucleation theory based on capillarity approximation \( \textbf{I} \)

\[ \frac{A}{kT} = \frac{16\pi}{3} \left( \frac{\gamma(T)}{kT} \right)^3 \frac{1}{\rho_f^2(T) \ln^2 s} \]  

(7)  

(the supersaturation \( s = \frac{p(\mathcal{E})}{p(T)} \) characterizes the saturated vapour) are shown in Figures 3, 4. This quantity yields the nucleation rate \( J = J_0 \exp \left( -\frac{A}{kT} \right) \) which is measured in nucleation experiments in the cloud chamber or in the upward thermal
diffusion cloud chamber. Similarly to the surface tension the nucleation barriers appear to be field independent for given values of $\frac{T}{T_c} \left( \frac{|E|}{E_c} \right)$ and $\frac{p}{p_c} \left( \frac{|E|}{E_c} \right)$.

The results of a study of the nonuniform properties of atomic fluid in the electrical field presented in this report have been obtained within the frames of the standard density functional approach. The new point is the suggested density functional of the grand thermodynamic potential (4), (5). The main results concern the influence of electric field on the phase diagram (Figure 1), surface tension (Figure 2), gas–to–liquid and liquid–to–gas nucleation barriers (Figures 3, 4). These results may be useful for analysis of the corresponding experimental data (for example, for fluids of noble atoms) on the nucleation phenomena in the presence of the electrical field. However, it should be stressed that the analysis of the influence of the electric field on the nucleation phenomena in the concrete experiment requires a separate consideration that is out of the scope of the present paper. The presented theory exhibits a kind of universality: if the temperature and the pressure are measured in units of their critical values for a given strength of the electric field the results for the surface tension and nucleation barriers are field independent.

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