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New developments in nucleation theory and their impact on natural gas separation

Vitaly Kalikmanov, Marco Betting / Twister Supersonic Gas Solutions BV

Johannes Bruining, David Smeulders/ Delft University of Technology

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Abstract

Conventional separators in the oil industry use a feed of oil and gas in two-phase multi-component equilibrium. Recently a new concept of separators has been introduced which can be fed with a single-phase gaseous mixture. The separator combines a quasi-isentropic expansion of the gas during which liquid droplets are formed by the nucleation process and a gas-liquid cyclonic separator. The performance predictions of such a separator depend critically on an adequate description of nucleation phenomena. For a large number of practical cases the *Classical Nucleation Theory* is very inaccurate. The recently proposed *Mean-field Kinetic Nucleation Theory* yields quantitatively accurate predictions of nucleation behavior of various microscopically diverse substances. An important advantage of non-equilibrium separation is the minimal use of chemicals and absence of regeneration systems, as opposed to conventional separation methods such as glycol contactors or silica gel towers.

Introduction

A separator is used to separate gas, oil and water from the fluids produced in oil fields. The focus of this paper is on a new concept for natural gas separators. Conventionally the industry used vessel-type separators, in which gas is separated from the oil by gravity forces. Vessel separators are large, heavy and expensive in terms of the space that they occupy on offshore platforms. One attractive alternative appears to be the use of Gas-Liquid Cylindrical Cyclone (GLCC). For this

device the oil and gas phases are also already in equilibrium before entering the separator. It is essentially a cylindrical pipe in which a mixture of gas and liquid in thermodynamic equilibrium are injected tangentially, thereby causing a vortex. The gas-oil mixture is thus separated by centrifugal and buoyancy forces. The cylinder has two outlets, at the bottom and at the top, used for gas and oil respectively.

The introduction of GLCC technology started only in the early 1990's [1]-[3] when economic and operational pressures encouraged the use of less expensive and more efficient separators, especially for offshore applications. However, in 1996 only 45 GLCC's were used world-wide in oil production facilities, mainly because the theory from which the design criteria could be computed was not well established, and LCO (liquid carry over) and GCU (gas carry under) were unpredictable. Since then the hydrodynamic theory for GLCC's has gradually been established [4]-[5]. As the mechanistic model was improved, a design code [6] could be formulated and the number of field applications increased considerably. The optimal performance is, however, constrained because the feed stream in conventional GLCC's is typically a *two-phase* mixture at equilibrium conditions. The dispersed phase (being liquid droplets, bubbles or solid particles) is separated using the inertia of the heavier phase, but generally no phase transition occurs. Note that the separation of water in conventional devices frequently requires the use of chemicals [7].

In the present paper we are not aiming at optimizing GLCC but at introducing a completely *new concept of a gas-liquid separator*. Instead of the conventional scheme operating under equilibrium conditions, one can think of a device based on a very different physical mechanism, namely, *nonequilibrium phase transitions* [8]. In such a device, the feed stream is generally a *single-phase* multi-component gaseous mixture containing condensable vapors. The gas flows through a separation section, representing a Laval nozzle, at supersonic velocity. Three main physical processes are:

- A near isentropic expansion of the gas in the nozzle resulting in a drop of temperature and pressure due to the high (supersonic) velocity

- Nucleation of vapors induced by the fast expansion resulting in the formation of fine mist of sub-micron (usually, nano-sized) clusters, which then grow by means of diffusion and coalescence and/or coarsening (Ostwald ripening) to macroscopic droplets
- Separation by inertia of the droplets heavier than the surrounding gas due to a strong swirling flow



Figure 1: Artist impression of the “Twister Supersonic Separator”. The flow direction is from left to right. The separated liquid and slip gas are transported towards the bottom. The dry gas is continuing to the right.

Figure 1 shows an artist’s impression of such a device - the “Twister Supersonic Separator” [8]. Natural gas entering from the left is led over a stationary inner body with swirl imparting vanes in an annulus at the maximum width of the inner body. The inner body then contracts and due to conservation of the angular momentum the tangential flow rate increases dramatically. As the tangential velocity increases with the reduction of the inner body diameter, the axial velocity component is also increased by the shape of the outer contour resembling a supersonic nozzle contour. A non-equilibrium (*supersaturated*) state is reached. From the thermodynamic point of view this state is *metastable* and results in *nucleation* – a spontaneous formation (due to thermal fluctuations) of embryos of the liquid phase (*critical clusters*). The degree of metastability is characterized by the difference between the chemical potentials of the supersaturated vapor and the liquid at the same pressure and temperature, $\Delta\mu > 0$.

Clusters formed during nucleation grow by diffusion and become small droplets that, due to the high rotational forces, are driven towards the outer sidewall of the tube. A simple vortex finder then separates the dry core flow from the liquid and the slip gas flowing along the wall. After the separation phase the two streams are decelerated in order to recover the kinetic energy into pressure in two concentric diffusers.

For the non-equilibrium separator, the theory to predict its performance is more difficult than for a conventional separator. In the non-equilibrium separator the key process giving rise to gas separation is nucleation. It is also the most sensitive part of the theoretical modelling. For non-equilibrium separators, this implies that one has to possess a reliable nucleation model for the common natural gas substances for a versatile application in the field. This paper shows that recent advances in nucleation theory make it possible to come to reliable operating conditions for the separator. This is validated against experimental data obtained by various world-wide research groups.

After a brief discussion of the classical approach to nucleation (classical nucleation theory) focusing on its advantages and disadvantages, a short discussion is presented of an alternative model (mean-field kinetic nucleation theory) that has recently been formulated. A comparison of both classical and new

theory predictions with the available experimental data for the substances of interest for gas-separation in oil recovery applications will be presented, followed by the challenges faced in nucleation modelling. One of the main challenges is application of the nucleation theory to long chain molecules (e.g., heavy hydrocarbons). Another challenge is to accurately take into account the strong real gas effects occurring in natural gas under high pressure.

Modelling nucleation: shortcomings of Classical Nucleation Theory and new developments. Mean-field Kinetic Nucleation Theory

The most widely used description of nucleation phenomenon is the Classical Nucleation Theory (CNT) of Becker-Döring-Zeldovich (for a review see [9]). It is based on the so-called “*capillarity approximation*.” Its essence is that small clusters causing nucleation of the bulk liquid from the vapor are treated as macroscopic spherical objects. It means that they have a well defined radius R , the bulk liquid density inside the droplet and the bulk vapor density outside it. The free energy of formation of a n -cluster, $\Delta G(n)$, where n is the number of molecules in the cluster, contains the negative bulk term ($-n\Delta\mu$) and a positive surface term due to the energy necessary to build a surface of a cluster; the latter contains the product of the plain layer vapor-liquid surface tension γ_∞ and the surface area of the cluster which scales as $n^{2/3}$. At small n , the positive surface term dominates making it energetically unfavorable to create a very small cluster in view of the large uncompensated surface energy. For large n , the negative bulk contribution prevails. The maximum of $\Delta G(n)$ corresponds to the critical cluster n_c (see Fig. 2). It represents a free energy barrier which a system has to overcome to form a new stable (liquid) phase. Clusters with $n < n_c$ molecules dissociate whereas those with $n > n_c$ grow into the new phase.

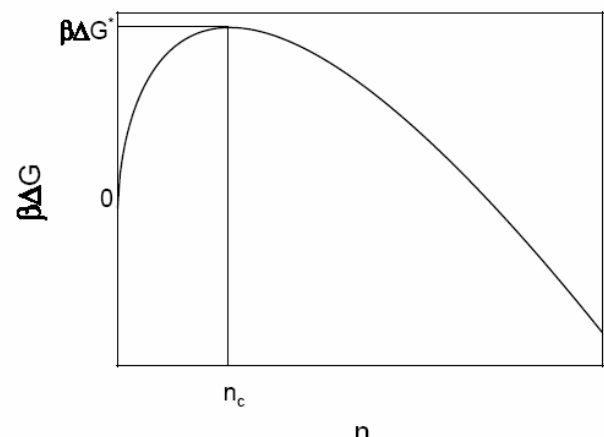


Figure 2. Behavior of the Gibbs free energy of the cluster formation, $\Delta G(n)$, in the Classical Nucleation Theory, as a function of the number of molecules n in the cluster (here $\beta=1/k_B T$, T is the temperature and k_B is the Boltzmann constant).

It is clear that by construction CNT is a phenomenological theory and as such is only applicable to large clusters. When the critical cluster becomes small the purely phenomenological considerations lose their validity. Indeed, in a number of nucleation experiments ([10]-[13]) it was found that CNT failed to predict nucleation rates by many orders of magnitude. At the actual conditions within a non-equilibrium, natural gas separator, the *nucleation rate* - the number of critical clusters formed per unit volume per unit time - becomes very high (typically $\sim 10^{12} - 10^{14} \text{ cm}^{-3} \text{ s}^{-1}$), while the typical size of the cluster is of the order of a few nanometers. This is the range where CNT becomes invalid.

In this situation a semi-phenomenological approach appears to be a promising alternative, especially as far as nucleation in complex substances is concerned. It represents a combination of statistical thermodynamics of clusters with thermodynamic data on equilibrium material properties. Recently one of us has formulated such a model - *Mean-field Kinetic Nucleation Theory* (MKNT) [14] - which is applicable to clusters of arbitrary sizes down to monomers. The model contains two surface tensions; the macroscopic (planar), γ_{∞} , dominating the behavior of large clusters, and microscopic, γ_{micro} , dominating the behavior of small clusters. Both of them contribute to the behavior of clusters of intermediate sizes. The γ_{micro} is a temperature dependent quantity which is obtained from the vapor compressibility factor at saturation, without the reference to microscopic interactions (for the details see Ref. [14]).

MKNT has been verified in independent experiments, carried out on a world-wide basis, in such microscopically diverse substances as argon, nitrogen, water, and mercury, demonstrating very good agreement with experimental data. For the natural gas applications the accurate prediction of water nucleation is of great importance: removing water is critical to preventing clathrates formation which is vital to the success of supersonic separator technology and efficient natural gas recovery. Recently, two experimental groups, Wolk et al. [15] and Labetski et al. [13] reported the results of nucleation experiments for water in the wide temperature range of 200-260 K. These conditions are close to those occurring in natural gas separators. Though the two groups used different experimental techniques - an expansion chamber in [15] and a shock wave tube in [13] - the results obtained by them are consistent.

Figure 3 shows the relative nucleation rate; that is the ratio of experimental data to theoretical predictions $J_{\text{rel}} = J_{\text{exp}}/J_{\text{th}}$. Closed symbols correspond to MKNT, open symbols to CNT. Circles are experimental results of Wolk et al., squares from experiments of Labetski et al. Also shown is the "ideal line" (dashed line); $J_{\text{exp}}=J_{\text{th}}$. (if a theory would be ideal all the points should have fallen on this line). The results are presented on the \log_{10} scale.

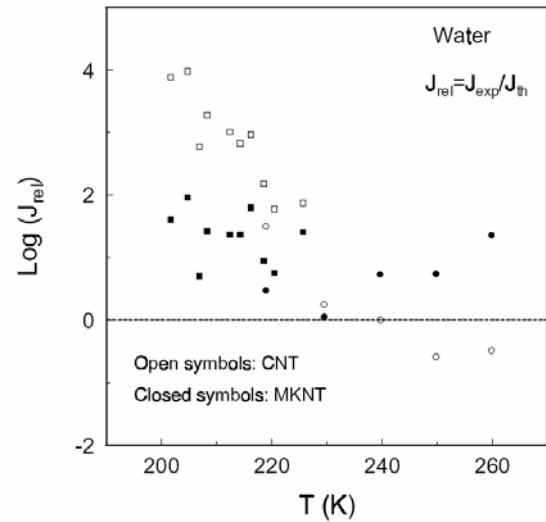


Figure 3. Relative nucleation rate for water. Closed symbols correspond to MKNT, open symbols - to CNT. Circles are experimental results of Wolk et al. [15], squares - experiment of Labetski et al. [13]. Also shown is the "ideal line" (dashed line): $J_{\text{exp}}=J_{\text{th}}$. The results are presented on the \log_{10} scale.

Across the whole temperature range the MKNT predictions are 1-2 orders of magnitude off the experimental data, while the CNT results are up to 4 orders of magnitude lower. The most important observation is that MKNT predicts *the temperature dependence* of the nucleation rate correctly. The relative MKNT nucleation rate remains approximately constant as the temperature changes, while the CNT underestimates the nucleation rate at lower temperatures and overestimates it at higher temperatures. This is not surprising since the critical cluster at these conditions contains approximately 15-20 molecules, implying that the phenomenological approach is essentially in error. Note that for such small clusters the very concept of a (macroscopic) surface tension, playing the crucial role in the capillarity approximation, is not defined and microscopic considerations become a necessity.

The most striking difference between the CNT and MKNT predictions are obtained for mercury nucleation. Some natural gas fields contain mercury and its removal is of vital importance, due to health and environmental issues. The problem of mercury removal is discussed in the paper [16] presented at this Conference. The planar surface tension of mercury is about 6-8 times higher than that of molecular fluids. As a result, the vapor-liquid nucleation requires a very high supersaturation to compensate for the energy cost to build the cluster surface. Another important feature of mercury (typical for liquid metals) is that its electronic structure strongly depends on the thermodynamic state, implying that the interatomic interactions depend on the thermodynamic state. Mercury vapor is a simple rare-gas system with only Van der Waals dispersive interactions. However, being combined in clusters, mercury atoms behave differently. Beyond a certain cluster size the energy gap becomes smaller

than $k_B T$, resulting in the nonmetal-to-metal transition. Experimental study of mercury nucleation in helium as a carrier gas was carried out by Martens, Uchtmann and Hensel [12]. The measurements were made in an upward diffusion cloud chamber. The supersaturation S giving rise to the onset of nucleation is referred to as the *critical supersaturation*. Figure 4 shows the experimental results (closed circles) for the critical supersaturation S at different temperatures. Also shown are predictions of the MKNT (solid line) and the CNT (dashed line). Calculations were performed for the conditions below the non metal-to-metal transition. MKNT results are in very good agreement with experiment while the CNT predictions for S are about 3 orders of magnitude higher than the measured values of S . This discrepancy in S gives rise to an extremely high discrepancy in nucleation rate; for example, for the experimental nucleation point $T=284\text{ K}$, $\ln S=9.35$ (where $J_{exp}=1\text{ cm}^{-3}\text{s}^{-1}$) the predicted CNT nucleation rates are extremely small: $J_{CNT}=10^{-67}\text{ cm}^{-3}\text{s}^{-1}$, deviating from experiment by about 67 orders of magnitude! Meanwhile MKNT gives reasonably accurate predictions: $J_{MKNT}=10^3\text{ cm}^{-3}\text{s}^{-1}$.

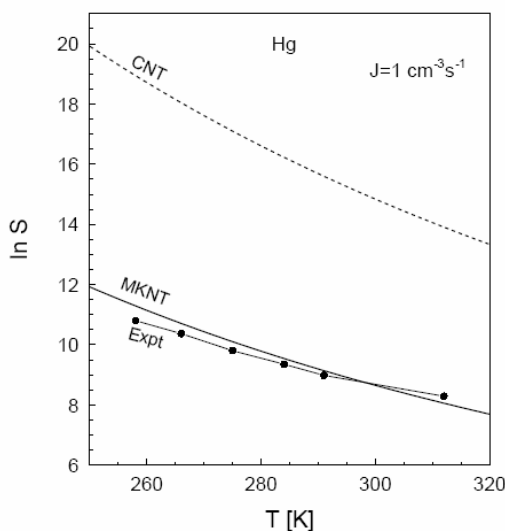


Figure 4. Critical supersaturation of mercury vapour corresponding to $J_{exp}=1\text{ cm}^{-3}\text{s}^{-1}$ as a function of the nucleation temperature. Closed circles – experiment of [12]. Solid line – corresponds to MKNT, dashed line – to CNT.

Challenges in nucleation modelling

It is well known that an efficient separation of heavy hydrocarbons is an important requirement for natural gas separators. From the physical (molecular) point of view hydrocarbons represent chain-like molecules. The molecular description of such substances is much more complex than that of *simple fluids*, which have spherical molecules. Recently, MKNT has been extended to include the properties of chain-like molecules [17]. This extension is a combination of the original MKNT of Ref. [14] with the Statistical Associating Fluid Theory (SAFT) (for a review of SAFT see Ref. [18]). At present MKNT can be applied to nucleation in

an arbitrary *n*-alkane; the additional input parameter of the model is the molecular weight of the *n*-alkane molecule. Nucleation of heavy hydrocarbons at high pressures – typically separators have nucleation pressures around 30-80 bar – is a very complicated process due to the presence of strong real gas effects. These effects are responsible for the active role played by light components (like methane) which otherwise could have been considered as inert carrier gas which does not take part in the nucleation process. In experiments on nucleation of n-nonane/methane mixture, performed in Eindhoven University of Technology (Netherlands) [19]-[21] it was found that at high pressures the critical cluster consists primarily of the methane molecules with a very small amount of nonane. At $T=240\text{ K}$ and total pressure 40 bar, the critical cluster contains only 5 nonane molecules and about 35 methane molecules. Considerations based on the CNT are not able to describe this effect even qualitatively. In fact, CNT predicts the opposite trend. Recently an explanation of this anomalous behavior has been proposed [22]. It has been shown that it is a manifestation of the dominant role of the *unlike interactions* (i.e. nonane-methane) at high pressures resulting in the *negative partial molar volume* of nonane in the vapor phase which occurs beyond the so called “compensation pressure”. The *compensation pressure effect* strongly suggests the necessity of applying a multi-component nucleation model for such mixtures at high pressures. Such a model is now being developed.

Conclusions and significance

- Recent developments in nucleation theory has allowed the design, test and commercialisation of a new generation of gas-oil separators, based on non-equilibrium phase transitions; namely the *Twister* supersonic gas separator.
- The recently proposed *Mean-field Kinetic Nucleation Theory* [14] yields quantitatively accurate predictions of nucleation behavior of various microscopically diverse substances
- At high pressures it is necessary to develop a nucleation model taking into account strong real gas effects
- The new separation (*Twister*) technology based on non-equilibrium phase transitions allows the reduction of undesirable components in the gas phase, which would otherwise need transportation via pipelines or storage.
- An important advantage of non-equilibrium separation is the absence regeneration systems and minimal use of chemicals as opposed to conventional separation – of real importance to the current environmental sensitivities
- Non-equilibrium separators can be used for dewpointing and condensate recovery in upstream and midstream application.

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