A SIMPLE THEORY OF CONDENSATION

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A simple assumption of an emergence in gas of small atomic clusters consisting of c particles each leads to a phase separation (first-order transition). It reveals itself by the emergence of a "forbidden" density range starting at a certain temperature. Defining this latter value as the critical temperature predicts the existence of an interval with the anomalous heat capacity behavior $c_p \propto \Delta T^{-1/c}$. The value $c = 13$ suggested in the literature yields the heat capacity exponent $\alpha = 0.077$.

1. INTRODUCTION

The theory of gas–liquid condensation is probably the most famous unsolved problem in classical statistical mechanics [1]. Numerous attempts to attack the problem have been made during the last hundred years. They were based on a wide range of different techniques, from cumulant expansion to field theory methods of phase transitions [2]. A considerable step in this direction was made by the cluster (droplet) theory of Fisher [3]. This theory predicts an essential singularity of the free energy at the condensation point.

A simple model of condensation that opens the way to the appearance of a critical point and the corresponding phase separation is suggested here. This model reveals the basic desirable features of the condensation and allows a new and self-consistent definition of the critical point. Moreover, it identifies the famous heat capacity singularity and explains it up to the calculation of the divergency exponent in an excellent accordance with the measured data.

Isolated clusters of atoms and molecules have been observed in molecular beams experimentally and studied theoretically [4]. Stability of such clusters has also been studied in a liquid-like environment in [5]. It was shown there that the locally preferred structure of the Lennard–Jones liquid is an icosahedron (13 atoms), and that the liquid-like environment only slightly reduces its relative stability.

Scattering experiments can also be regarded as an additional indirect argument in favor of clustering in liquids. For example, the argon radial distribution function [6] shows neither temperature nor density dependence of the abscissa of its first maximum, which means that the internuclear distances in solid, liquid, and gaseous argon are inherent characteristics of the material. In other words, this phase independence can be attributed to the persistence of small dense clusters.

A more detailed study of experimental evidence in favor of the existence of relatively stable small atomic clusters will be published elsewhere [7].
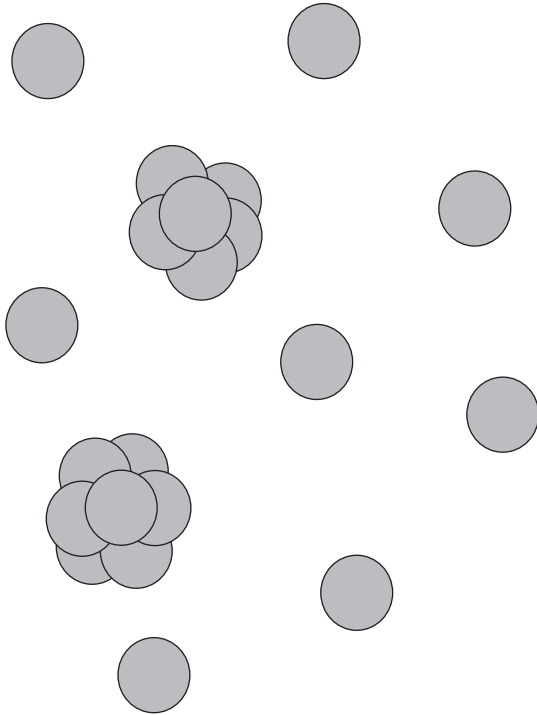
2. BASIC ASSUMPTION

Based on the foregoing, it is possible to formulate the following basic assumption: elementary particles of a gas (atoms or molecules) form small, relatively stable clusters consisting of c particles each. Their concentration is a function of state. It then immediately follows that the gas should be regarded as (at least) a two-component system (see the Figure).

The ground state of the system under consideration is expected to be a full separation as the energetically preferable configuration (we do not address those special cases where geometry allows packings denser than the FCC or HCP ones). On the other hand, at high temperature, the system remains a mixture of atoms and clusters. Hence, separation into two phases occurs at a finite temperature.

This observation helps us answer a very natural question: why do we suppose clusters of only one size to form or, at least, to be stable. Unfortunately, we do not know an *a priori* reason for this. On the other hand, as we see, the existence of clusters of one size leads to the separation. Therefore, the existence of clusters of any different number of particles would reveal itself

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through multiple separations. To the best of our knowledge, it is not the case with simple liquids in Nature. This *a posteriori* argument therefore justifies our basic assumption. Incidentally, the complicated phase diagrams of complex liquids may be attributable to the existence of clusters of different sizes and nature.

Such a model reveals a universal behavior. Indeed, a close vicinity of the critical point (if it exists) has to be governed by the universal properties of the two-component mixture separation, regardless of the specific details of the inter-particle interaction. That interaction affects the critical parameters, i. e., physical coordinates, but not the system behavior.

Our basic assumption plays a role analogous to that of the Cooper pairing in an early version of the superconductivity theories: it is a microscopic phenomenon underlying the macroscopic one. Knowledge of the exact (probably, quantum) mechanism of this clustering is not crucial to understand the liquid–gas transition.

3. FREE ENERGY

We start with the expression for the Helmholtz free energy for a two-component slightly nonideal gas mixture [8]

$$\beta F = N_1 \ln \left(\frac{\lambda_1^3}{e} \frac{N_1}{V} \right) + N_2 \ln \left(\frac{\lambda_2^3}{e} \frac{N_2}{V} \right) + \beta E_B N_1 + $$
$$+ \frac{1}{V} \left(B_{11} N_1^2 + 2 B_{12} N_1 N_2 + B_{22} N_2^2 \right). \quad (1)$$

Let $N_1 = n$ be the number of clusters containing c particles each; $N_2 = N - cn$, and N be the total number of particles; $\beta = (k_B T)^{-1}$, as usual. As already noted, we assume that all the clusters have the same and constant number of constituent particles, c. The value

$$\lambda_i = \sqrt{\frac{2\pi\beta}{m_i}}\,\hbar$$

is a thermal wave length and m_i is a particle mass. E_B stands for a cluster binding energy and B_{ij} denote second virial coefficients. Thus,

$$\beta F = n \ln \left(\frac{\lambda_1^3}{e} \frac{n}{V} \right) + (N - cn) \ln \left(\frac{\lambda_2^3}{e} \frac{N - cn}{V} \right) + $$
$$+ \beta E_B n + \frac{1}{V} B(\beta; n), \quad (2)$$

and the internal energy is

$$U = \left(\frac{\partial(\beta F)}{\partial \beta} \right)_V = \frac{3}{2} \frac{1}{\beta} [N - (c - 1)n] + $$
$$+ E_B n + \frac{1}{V} B'_\beta(\beta; n), \quad (3)$$

where

$$B(\beta; n) \equiv B_{11}(\beta) n^2 + 2 B_{12}(\beta) n(N - cn) + $$
$$+ B_{22}(\beta)(N - cn)^2. \quad (4)$$

Within the same approximation (a slightly nonideal mixture), the equation of state is [8]

$$P\beta = \frac{1}{V} [N - (c - 1)n] + \frac{1}{V^2} B(\beta; n). \quad (5)$$

A dynamic equilibrium configuration of the two-component system is defined by the value of n corresponding to the minimum of the total free energy. Simple differentiation of Eq. (2) leads to the main equation for n:

$$\ln \left(\lambda_1^3 \frac{n}{V} \right) - c \ln \left(\lambda_2^3 \frac{N - cn}{V} \right) + $$
$$+ \beta E_B + \frac{1}{V} B'_n(\beta; n) = 0, \quad (6)$$

or

$$\ln \left(\lambda^3 x \rho \right) - c \ln \left(\lambda^3 \rho (1 - cx) \right) - $$
$$- \frac{3}{2} \ln c + \beta E_B + \rho B'_x(\beta; x) = 0, \quad (7)$$

where

$$\rho \equiv \frac{N}{V}, \quad x \equiv \frac{n}{N}, \quad \lambda = \lambda_2, \quad \lambda_1 = c^{-1/2}\lambda,$$

$$B(\beta; x) = B_{11}x^2 + 2B_{12}x(1 - cx) + B_{22}(1 - cx)^2.$$

One has to solve Eq. (7) analytically, i. e., to find $x = x(\rho)$. Instead, we found an inverse function, $\rho = \rho(x)$, where $x \in [0, 1/c]$. This is easily done with the aid of the Lambert W-function [9] (ω-function in another notation):

$$\lambda^3 \rho = \left[\frac{ax}{(1 - cx)^c} \right]^{1/(c-1)} \times$$

$$\times \exp \left\{ -W \left(-\left[\frac{ax}{(1-cx)^c} \right]^{1/(c-1)} \frac{B'_x(\beta; x)}{(c-1)\lambda^3} \right) \right\}, \quad (8)$$

where

$$a = c^{-3/2} \exp(\beta E_B).$$

In fact, equation of state (5) in the form

$$P\beta = \rho[1 - (c - 1)x] + \rho^2 B(\beta; x) \quad (9)$$

and Eq. (8) define $P(\rho)$ using the parameter x.

The most interesting feature of Eq. (8) is the existence of "forbidden" values for ρ. This behavior is governed by the sign of the derivative $B'_x(\beta; x)$. Namely, if for a given β it remains negative for all permissible values of x, then ρ ranges over the entire positive semi-axis. This is clear from the behavior of the Lambert function in the negative range [9]. If the expression changes its sign to positive, an equilibrium solution jumps from the W_0 branch, continued from the positive argument, to the W_{-1} one. Moreover, the positive range of the expression has another "forbidden" region because the absolute value of the Lambert function negative argument cannot exceed $1/e$.

4. THE CRITICAL POINT

The standard definition of a critical point is

$$\left(\frac{\partial P}{\partial \rho} \right)_\beta = \left(\frac{\partial^2 P}{\partial \rho^2} \right)_\beta = 0. \quad (10)$$

However, this definition is not applicable if a singularity is expected to be revealed at this point. Moreover, as we just saw, there exists some special behavior characterized by the sign of $B'_x(\beta; x)$. Thus, the very last (critical) point before the ρ axis becomes "teared up" is defined by $B'_x(\beta_c; x_c) = 0$. In fact, this equation defines critical parameters: the (inverse) critical temperature β_c and the critical concentration x_c, satisfying

$$[B_{12}(\beta_c) - cB_{22}(\beta_c)] +$$

$$+ x_c[B_{11}(\beta_c) - 2cB_{12}(\beta_c) + c^2 B_{22}(\beta_c)] = 0. \quad (11)$$

The left-hand side consists of smooth monotonic functions of β (second virial coefficients) and is linear in x, and hence attains its extremum at a limiting point. It cannot be $x_c = 0$ because our physical system is supposed to be stable at small concentrations. Therefore, the only possibility is $x_c = 1/c$, and Eq. (11) becomes

$$B_{11}(\beta_c) - cB_{12}(\beta_c) = 0. \quad (12)$$

The root β_c of this equation is the inverse critical temperature. Naturally, these equations for x_c and β_c are strongly depend on the approximation. A higher viral expansion would complicate Eq. (11), leading to different values for the roots x_c and β_c.

An important observation to make here is that the atom–cluster (B_{12}) and cluster–cluster (B_{22}) interactions should be substantialy weak in comparison with the interatomic one (B_{11}), because part of the gas energy is accumulated in the cluster bindings. This results, in turn, in a "shallow" potential well with a much shorter repulsive part and a relatively small intercluster distance, and then in a much higher density of the heavy component of the gas.

This new definition of the critical point, $B'_x(\beta_c; x_c) = 0$, allows writing an expansion in the vicinity of this point,

$$B'_x(\beta; x) \approx B''_{x\beta}(\beta_c; x_c)\Delta\beta + B''_{xx}(\beta_c; x_c)\Delta x, \quad (13)$$

where $\Delta\beta \equiv \beta_c - \beta$ and $\Delta x \equiv x_c - x$. Substituting this, $x \to 1/c$, $\beta \to \beta_c$, and $1 - cx \to c\Delta x$ in Eq. (7), we obtain the main eguation (7) in a close vicinity of the critical point

$$c \ln (\Delta x) - cA = \rho B''_{xx} \Delta x, \quad (14)$$

where

$$cA \equiv \rho B''_{x\beta}\Delta\beta + \beta_c E_B - (c-1)\ln \left(\lambda_c^3 \rho \right) + \left(c - \frac{5}{2} \right) \ln c.$$

This equation is solved as before with the aid of the Lambert function and its solution is given by

$$\Delta x = e^A \exp \left\{ -W \left(-\frac{1}{c}\rho B''_{xx} e^A \right) \right\} \quad (15)$$

with

$$e^A = \left(\lambda_c^3 \rho \right)^{1-1/c} c^{1-5/2c} \exp \left\{ \frac{1}{c} \left(\beta_c E_B + \rho B''_{x\beta}\Delta\beta \right) \right\}.$$

This looks like an ultimate solution of the problem, in the vicinity of the critical point at least, but it does not account for the basic feature — the discontinuity of the ρ-scale — and it should be used very carefully.

5. SPECIFIC HEAT

The internal energy is given by

$$\frac{U}{N} = \frac{3}{2}\frac{1-(c-1)x}{\beta} + E_B x + \rho B'_\beta(\beta; x) \qquad (16)$$

and the specific heat, by

$$c_V = \frac{\partial}{\partial T}\left(\frac{U}{N}\right)_V = -k_B \beta^2 \frac{\partial}{\partial \beta}\left(\frac{U}{N}\right)_\rho =$$

$$= k_B \left\{\frac{3}{2}[1-(c-1)x] - \rho\beta^2 B''_{\beta\beta}\right\} +$$

$$+ k_B \beta \left\{\frac{3}{2}(c-1) - \beta E_B - \rho\beta B''_{x\beta}\right\} x'_\beta. \quad (17)$$

Therefore, if we look for special behavior of this quantity in the vicinity of the critical point, then x and x'_β have to be examined. We also use the fact that on the critical isohore, c_V behaves like c_p in a second-order phase transition [10].

We start with substituting Eq. (13) in Eq. (8) and then note that

$$B''_{xx}(\beta_c; x_c) = B_{11}(\beta_c) - 2cB_{12}(\beta_c) + c^2 B_{22}(\beta_c) =$$
$$= B_{12}(\beta_c) - cB_{22}(\beta_c).$$

This represents the cluster–atom and cluster–cluster interactions, which are supposed to be very small. Hence, we can expect the existence of an interval where $B'_x(\beta; x) \approx B''_{x\beta}(\beta_c; x_c)\Delta\beta$ and

$$\ln\left(\lambda_c^3 \rho\right) = \ln\left[\frac{a_c/c}{(c\Delta x)^c}\right]^{1/(c-1)} -$$

$$- W\left(-\left[\frac{a_c/c}{(c\Delta x)^c}\right]^{1/(c-1)}\frac{B''_{x\beta}(\beta_c; x_c)}{(c-1)\lambda_c^3}\Delta\beta\right). \quad (18)$$

Further consideration depends on the sign of $B''_{x\beta}(\beta_c; x_c)\Delta\beta$. In the homogeneous phase, it is negative, and we are on the W_0 branch with a small positive argument. Here, it suffices to take $W_0(y) \approx y$ [9] and, subsequently,

$$\lambda_c^3 \rho = \left[\frac{a_c/c}{(c\Delta x)^c}\right]^{1/(c-1)} \times$$

$$\times \left\{1 - \left[\frac{a_c/c}{(c\Delta x)^c}\right]^{1/(c-1)}\frac{B''_{x\beta}(\beta_c; x_c)}{(c-1)\lambda_c^3}\Delta\beta\right\}.$$

The relevant root behaves as

$$\left[\frac{(c\Delta x)^c}{a_c/c}\right]^{1/(c-1)} \approx \frac{B''_{x\beta}(\beta_c; x_c)}{(c-1)\lambda_c^3}\Delta\beta$$

$$\text{or} \qquad \Delta x \propto (\Delta\beta)^{1-1/c}.$$

This means that the derivative $\Delta x/\Delta\beta$ and therefore the specific heat show the famous dependence

$$c_p \propto (\Delta\beta)^{-1/c}.$$

In view of the previous suggestion, $c = 13$, this exponent becomes $\alpha \approx 0.077$.

An analogous calculation cannot be done for a non-homogeneous phase because an equilibrium solution does not exist in this region.

6. CONCLUSIONS

A model that explains basic features of condensation is presented. The simple assumption of a relative stability of only one type of clusters statistically emerging in the gas immediately leads to a first-order phase transition (phase separation) at some finite temperature. It is experimentally observed as a condensation process.

We stress again that this model is by no means a simplified version of Fisher's model.

Mathematically, the condensation reveals itself as a forbidden density (volume) region. The density jumps from its gaseous value to the liquid one. No intermediate values are allowed. A corresponding region for the Van der Waals equation is the well-known S-shaped instability. It needs a special auxiliary construction to be treated as a metastable state.

This paper presents a new concept of the critical point: it is a point of the density continuity failure. This definition coincides graphically with the old one but it allows constructing a convenient expansion in the close vicinity of the point under consideration. It demonstrates the famous singularity with the exponent $\alpha \approx 0.077$ that is in excellent agreement with known data.

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