Investigation of the gas density, the liquid density and the gravitational effect in the critical region of C$_6$F$_6$

E E Ustyuzhanin$^1$, V F Ochkov$^1$, V A Rykov$^2$ and S V Rykov$^2$

$^1$ National Research University Moscow Power Engineering Institute, Krasnokazarmennaya 14, Moscow 111250, Russia
$^2$ ITMO University, Kronvergskiy 49, Saint-Petersburg 197101, Russia

E-mail: evgust@tgmail.com

Abstract. Some thermodynamic functions are considered in the work. They have a scaling form and connected with thermodynamic properties at the saturation line (the fluid density ($\rho_l$), the gas density ($\rho_g$), the order parameter, the mean diameter of the coexistence curve, etc). We have paid attention to well-known experimental ($\rho_l$, $\rho_g$, $T$) data of C$_6$F$_6$, which are got in a wide temperature interval. One more object is investigated in the work. It is a height dependence of the density, $\rho(h)$, in the critical region, here $h$ is the distance of the gamma-ray beam from the bottom of the cell, in which the sample is placed. These ($\rho$, $h$, $T$) data are got at the earth gravity ($g = 9.8 \text{ m/s}^2$). In our work, it is studied a behavior of the sample at a special condition: the gravitational effect is reduced in the cell with the sample. In the case of the microgravity, we have elaborated an equation, which expresses a meniscus position in two-phase sample in the critical region. Combined models are elaborated to approximate ($\rho_l$, $\rho_g$, $T$) data of C$_6$F$_6$ in the wide temperature interval including the critical region. These models meet the scaling theory of critical phenomena.

1. Introduction

Experimental ($\rho_l$, $\rho_g$, $T$) data have been received by Stankus et al [1] in the temperature range 298.79–516.57 K for C$_6$F$_6$. Their method uses a beam generated by a gamma source; in the experiment, the intensity of the beam is measured. The beam passes through the sample placed in the cell. The latter is a horizontal cylinder with the length of 140.0 mm and the diameter of 40.0 mm. The beam can move in the plane, which is perpendicular to the axis of the cylinder. The beam can move vertical from the bottom up. Along with ($\rho_l$, $\rho_g$, $T$) data, the method gives an opportunity to measure the following:

- a vertical distance, $h$, from the beam to the bottom of the cylinder;
- data on the gravitational effect or a dependence of the density distribution, $\rho(h)$, on isotherms (lines 3, 4 and 5, figure 1);
- the pressure, $P$, at the top part of the cylinder.

The experiments have showed that a gravitational component ($P_g = \rho gh$) makes a significant contribution to the pressure, $P$, measured. $P_g$ leads to the following conclusions [1]:
The experiment shows that the local density, $\rho$, may differ from calculated ($\rho_l$, $\rho_g$, $T$), for example, $\rho(h)$ differs from $\rho(h)$ by (2–10)\% depending on $h$ in interval 1 at $\rho > \rho_c$ (figure 1).

Of interest are next questions:

- A—Why $h_{MV}$ is not a function of the temperature?
- B—At what height, $h$, will the meniscus be placed in the cell under the following boundary conditions:
  - the average density, $\rho_{cell}$, follows to the equality $\rho_{cell} = \rho_c$, here $\rho_{cell}$ is the density related to the sample in the cell;
  - the temperature $T$ follows to the inequality $T < T_c$, for example, $T = 516.28$ K;
  - the gravitational effect is significantly reduced (for example, by mixing the example) in the upper part of the cylinder; the equilibrium density is equal to $\rho_g(T)$;
  - the gravitational effect is significantly reduced in the low part of the cell; the equilibrium density is equal to $\rho_l(T)$;
  - a meniscus is formed in the cell due to the finite difference of $(\rho_l(T), \rho_g(T))$?

In the work, we have set a number of tasks also:

- to investigate the position of the meniscus at the microgravity in the cell described in [1];
- to adjust ($\rho_l$, $\rho_g$, $T$) data accordingly to the meniscus positions in interval 1.

Another challenge is the development of adequate models, which will describe functions $\rho_l(\tau)$, $\rho_g(\tau)$, $f_d(\tau)$, $f_s(\tau)$, etc) in the critical domain of C$_6$F$_6$; these models have to meet the scaling theory of critical phenomena (ST) and to refine previously known results [1] in the near-critical area.

2. Gravitational effect and assessment of meniscus positions in the cell

The method [1] aims to obtain ($\rho_l$, $\rho_g$, $T$) data at remarkable gravitational effect in interval 1; this method includes the following steps:

- it has been chosen experimental ($\rho, h$) data, which are related to interval 1 and placed from $h = 0$ up to 17 mm; these densities are higher than the critical density $\rho_c$ (see figure 1 below);
- these isothermal points have been extrapolated to the intersection point ($x$) with the level of $h_{MV}$, for example, it is level 6 and $x = 610.1$ kg/m$^3$ at $T = 516.57$ K;
- $\rho_l = 610.1$ kg/m$^3$ is included in table 1.
Figure 1. Distributions, $\rho(h - h_{MV})$, along isotherms related to interval 1 at $\rho > \rho_c$: 3, 4 and 5—experimental ($\rho, h - h_{MV}$) data at temperatures 515.98, 516.28, 516.57 K; 7, 8 and 9—$\rho_{midl}(h - h_{MV})$ at temperatures 515.98, 516.28, 516.57 K; 1—displacement $h_{t1}$; 2—displacement $h_{t2}$; 6—displacement $h_{t3}$.

Similarly, it has been chosen experimental low ($\rho, h$) data, which are related to interval 1, placed from $h = 22$ up to 40 mm and satisfy the inequality $\rho < \rho_c$. To calculate $\rho_g(T)$, these isothermal data have been extrapolated to the intersection point ($x'$) with the level of $h_{MV}$; for example, it is $x' = 491.5$ kg/m$^3$ at $T = 516.57$ K. The density, $\rho_g$, has been chosen as $\rho_g = 491.5$ kg/m$^3$ (table 1).

To answer question A, we have analyzed experimental ($\rho, h, T$) data in interval 1. The error is 0.5 mm related to $h$ in the experiment [1]. The order of the $h_t$ value is 1 mm. Due to the error, it is difficult to do following:

- to differentiate test $h$ points by temperature near the altitude, $h_M$;
- to determine $h_t$ values on the bases ($\rho, h, T$) data near the altitude, $h_M$.

To answer question B, let us consider the following process. In condition I of the process, a substance is immersed in a horizontally placed cylinder, which has a volume, $V$, and the ratio, $L/d$, follows to the inequality $L/d > 1$. A mass of the substance is equal $M$. In this state, the density, $\rho_{cell}$, follows to the equality, $\rho_{cell} = \rho_c$, its temperature follows to the equality $T_1 = T_c$ and there is no gravitational effect. Let us put the virtual horizontal plane, $S_v$, along the axis of the cylinder (its level is $h_{t0}$). We highlight the upper and lower parts, which have volumes, $V/2$.

Let us move the example to condition II. In the process, isochoric conditions are met:

- $\rho_{cell} = \rho_c$;
• $T_2 = T_c - \Delta T$, here $\Delta T > 0$. As a result of this process, a condensation occurs, the mass of the substance of the upper part is reduced by $\Delta M > 0$.

The plane $S_c$ moves a distance of $h_t$ to the phase boundary. The phase densities can be written as $(\rho_g, \rho_l) = (\rho_c + \Delta \rho_g \rho_c, \rho_c + \Delta \rho_l \rho_c)$, here $\Delta \rho_l = (\rho_l - \rho_c)/\rho_c$, $\Delta \rho_g = (\rho_g - \rho_c)/\rho_c$. We write $V$ as a function of the arguments $(\Delta M, \Delta \rho_g, \Delta \rho_l)$ in the form

$$V = \frac{1}{\rho_c + \Delta \rho_g \rho_c} + \frac{1}{\rho_c + \Delta \rho_l \rho_c}. \tag{1}$$

From (1), the function $\Delta M/M$ can be expressed as

$$\frac{\Delta M}{M} = \frac{\Delta \rho_l + \Delta \rho_g}{2} + \frac{\Delta \rho_l \Delta \rho_g}{\rho_c} \frac{1}{\Delta \rho_g - \Delta \rho_l}. \tag{2}$$

We introduce known functions for the mean diameter and the order parameter:

$$f_d = (\rho_l + \rho_g)(2\rho_c)^{-1} - 1 = (\Delta \rho_l + \Delta \rho_g)/2, \tag{3}$$
$$f_s = (\rho_l - \rho_g)(2\rho_c)^{-1} = (\Delta \rho_l - \Delta \rho_g)/2. \tag{4}$$

Let us substitute (3) and (4) in (2) and take into account equalities $\Delta \rho_g - \Delta \rho_l = -2f_s$, $\Delta \rho_g \Delta \rho_l = f_d^2 - f_s^2$. After the transformation, we get

$$\frac{\Delta M}{M} = \frac{f_s - f_d}{2f_s} - \frac{f_d^2}{2f_s}. \tag{5}$$

The change in the volume of the upper part is represented as

$$\Delta V_g = \left(\frac{M}{2} - \Delta M\right) \frac{1}{\rho_g} - \frac{V}{2}. \tag{6}$$

Using (5) and (6) after the transformation, we obtain a relative change in the volume, $\Delta V_g/V$, in the form

$$\frac{\Delta V_g}{V} = \left(\rho_c - \frac{\Delta M}{M}\rho_c\right) \frac{1}{\rho_c (1 + \Delta \rho_g)} - \frac{1}{2} \simeq \left(1 - \frac{\Delta M}{M}\right)(1 - \Delta \rho_g) - \frac{1}{2}. \tag{7}$$

We note the equality, $\Delta \rho_g = f_d - f_s$. Using (5) and (7) and transformations, we express the function, $\Delta V_g/V$, as

$$\frac{\Delta V_g}{V} = \frac{(f_d + f_s^2 - f_s)(1 + f_s - f_d)}{2f_s} - \frac{f_d - f_s}{2}, \tag{8}$$
$$\frac{\Delta V_g}{V} = \frac{f_d}{f_s}\left(\frac{1}{2} + \frac{f_d f_s}{2} + \frac{f_d f_s^2}{2} + \ldots\right). \tag{9}$$

Let us consider the following conditions: $\Delta V_g/V > 0$ and $f_s > 0$, that is, the volume of the upper part increases in the specified isochoric process. Under these conditions in the asymptotic temperature region ($\Delta T > 0$ is a small value), the inequality is satisfied in the form

$$f_d > 0. \tag{10}$$

In our opinion, conclusion (10) is obtained for the first time and is valid for any form of functions $f_d, f_s$ in the critical domain.

We write the ratio $\Delta V_g/V$ as an approximate function with the argument, $h_t$, in the form

$$\frac{\Delta V_g}{V} = \frac{h_t}{L^2 \pi d^3}. \tag{11}$$

We present the displacement, $h_t$, using (9) and (11) in the asymptotic range in the form

$$h_t = \frac{\pi d}{8} ur, \tag{12}$$

where $ur = f_d/f_s$ is a temperature function.

It follows from (12) that $ur$ complex can be used to calculate the displacement, $h_t$, which will take place in interval 1 at the microgravity.
where $D$ coefficients.

approach. In the first stage, a combined model is selected to represent $u_r$ with the help of $(f_s, f_d)$ [2–4]:

$$f_s = B_{d0} \tau^\beta + B_{s1} \tau^{\beta + \Delta} + B_{s2} \tau^{\beta + 2\Delta} + B_{s3} \tau^2 + B_{s4} \tau^3,$$

(13)

$$f_d = B_{d0} \tau^{1-\alpha} + B_{d1} \tau^{2\beta} + B_{d2} \tau^{1-\alpha + \Delta} + B_{d3} \tau^2 + B_{d4} \tau^3,$$

(14)

where $D = (T_c, \rho_c, \alpha, \beta \ldots)$ are the critical characteristics of the model, and $C = (B_{sl}, B_{dl})$ are coefficients.

We emphasize that there are no scaling models representing functions $f_s, f_d$, etc in the critical domain for $C_6F_6$.

The values of $C$ and $D$ from (13), (14) should be determined on the base of a nonlinear least squares method (NRMS) [4, 5] and experimental $(\rho_l, \rho_g, T)$ data of $C_6F_6$ [1].

At the second stage, the values of $C$ and $D$ are calculated using NRMS for models (13), (14). Among the values, there are $T_c = 516.65$ K, $\rho_c = 550.43$ kg/m$^3$, $\alpha = 0.131$, $\beta = 0.348$, $B_{d0} = 2.145$, $B_{d1} = 0.595$, $B_{dexp} = 0.1005$.

Functions $\rho_l(T, D, C)$, $\rho_g(T, D, C)$ have been built using the model (13), (14) in the form

$$\rho_l = (f_d + f_s + 1)\rho_c, \quad \rho_g = (f_d - f_s + 1)\rho_c.$$

(15)

It is accepted that condition II will take place in interval 1. We have determined following:

- $ur_{exp}$ values calculated on the bases of values, $D = (T_c, \rho_c)$, and experimental $(\rho_l, \rho_g)$ data (columns 1 and 2) [1];
- $h_{texp}$ values calculated with the help of experimental $ur_{exp}$ values and equation (12);
- $(ur, T)$ data on the bases of equations (13), (14);
- $(h_t, T)$ data on the bases of $(ur, T)$ data and equation (12).

Some results of these calculations are shown in table 1 including $(h_{t1}, \tau_1, h_{t2}, \tau_2, h_{t3}, \tau_3)$ data. In connection with question A, we underline:

- $h_t$ values are small in comparison with $\Delta h$ interval;
- we have got some first data on $h(T)$ function of experiment [1].

It was assumed that the height of the meniscus, $h_{MV} = 19.1$ mm meets the following boundary conditions:

- the sample temperature is $T_1 = 516.57$ K (the maximum temperature in the experiment [1]);
- the corresponding displacement is $h_{t1} = 0.079$ mm (table 1); the specified state corresponds to the argument $(h - h_{MV} + h_{t1} = 0)$ and line $\theta$ (figure 1).

| $\rho_l \ exp$ | $\rho_g \ exp$ | $\tau$ | $\rho_l$ | $\rho_g$ | $ur_{exp}$ | $h_{texp}$ | $h_t$ |
|---------------|---------------|------|--------|--------|-----------|-----------|-----|
| 670.3         | 433.7         | 0.001| 675.54 | 437.23 | 0.0126    | 0.19      | 0.208|
| 644.8         | 455.8         | 0.000| 640.29 | 453.49 | -0.002    | -0.03     | 0.158|
| 610.1         | 491.5         | 0.000| 609.27 | 496.73 | 0.005     | 0.079     | 0.079|

**Table 1.** Some results of the second design stage: $\rho_l$ and $\rho_g$ in kg/m$^3$; $h_t$ in mm.

3. Some numerical data on the densities and meniscus positions

To construct the function $h_t(T)$ in relation to the experiment [1], we propose the following approach. In the first stage, a combined model is selected to represent $ur$ with the help of $(f_s, f_d)$ [2–4]:

**Table 1.** Some results of the second design stage: $\rho_l$ and $\rho_g$ in kg/m$^3$; $h_t$ in mm.
Table 2. The parameters of models (13) and (14): \( \rho_c \) in kg/m\(^3\); \( T_c \) in K.

| \( \rho_c \) | \( T_c \) | \( \alpha \) | \( \beta \) | \( B_{s0} \) | \( B_{s1} \) | \( B_{s2} \) |
|-------|-------|-------|-------|-------|-------|-------|
| 550.77 | 516.65 | 0.12985 | 0.34799 | 2.14345 | 0.134753 | -1.253085 |
| \( B_{s3} \) | \( B_{s4} \) | \( B_{d0} \) | \( B_{dexp} \) | \( B_{d2} \) | \( B_{d3} \) | \( B_{d4} \) |
| 1.40842 | -0.897481 | 0.59485 | 0.09995 | 0.042626 | 1.490123 | -2.520365 |

On the bases of \((h_t, T)\) data, we have estimated the distribution, \( \rho(h - h_{MV} + h_t) \). It was accepted: \( \rho_l(T_1) \) meets the condition \( \rho_l(T_1) = \rho_{mid11} \) in the volume, \( V_l \). To get \( \rho_{mid11} \), a few steps are taken. Firstly, we have divided \( V_l \) into several sections, which have heights \((h_{t,i}, i = 1-N)\), here \( h_{t,N} = 19.1 \) mm. Secondly, the distribution, \( \rho(h - h_{MV} + h_l) \), is used to calculate \( M_{mid11} \). This characteristic is an average integral mass, which is placed in the interval from \( h = 0 \) to \( h = 19.1 \) mm in \( V_l \); as a result, the average value, \( \rho_{mid11} = M_{mid11}/V_l \), is determined as \( \rho_{mid11} = 606.49 \) kg/m\(^3\) (line 9, figure 1). It is possible to see the point of intersection a of this isochoric function with line 6 (figure 1).

Thirdly, distributions, \( \rho(h - h_{MV} + h_{t2}, i = 2 - N) \), \( \rho(h - h_{MV} + h_{t3}, i = 3 - N) \), are used to calculate \( \rho_{mid12} = 646.49 \) kg/m\(^3\) (line 8, figure 1) and \( \rho_{mid13} = 668.94 \) kg/m\(^3\) (line 7, figure 1) in interval 1 at \( \rho > \rho_c \). A similar method is accepted to determine \( \rho_{mid14}, T \) data in interval 1 at \( \rho < \rho_c \): \( \rho_{mid14} = 494.93 \) kg/m\(^3\), \( \rho_{mid22} = 456.29 \) kg/m\(^3\) and \( \rho_{mid32} = 435.03 \) kg/m\(^3\). The points of intersection b, c of these isochoric functions with lines 1 and 2 are seen in figure 1. Let us note that \( \rho_{mid1}, \rho_{mid2}, T \) data are determined with the help of a numerical integration taking into account a cylindrical form of the cell with the set sizes \((L, d)\). These results made it possible to form a modified array of \((\rho_l, \rho_g, T)\) data, of which includes following:

- experimental \((\rho_l, \rho_g, T)\) data \([1]\) with the exception of points related to the temperatures 515.98, 516.28, 516.57 K;
- \((\rho_{mid1}, \rho_{mid2}, T)\) data.

Finally, we have calculated the parameters \((C, D)\) included in (13), (14) on the basis of the modified data array and NRMS methodology (table 2).

Answering question B, we indicate that the displacement corresponds to \( h_l = 0.158 \) mm at \( T = 516.28 \) K. The experimental density in this state corresponds to \( \rho_l = 644.8 \) kg/m\(^3\) and the calculated value is \( \rho_l = 646.83 \) kg/m\(^3\).

Let us underline that the structure of \( f_d \) (13) contains scaling components including a term, \( B_{dexp} r^{23} \), which has 23 index and \( B_{dexp} > 0 \) (see (10)). These features reflect current trends of ST \([2-4, 6]\). It is calculated \((\rho_l, \rho_g, T)\) data with the help of (15) at temperatures, which are related to interval 1 and interval 2. Local deviations, \( \delta \rho = 100(\rho - \rho_{(15)})/\rho \), are determined (figure 2) for \( \rho_l, \rho_g \) values included in the modified array, here \( \rho_{(15)} \) is a value calculated with the help of (15).

Let us consider one more condition III of the substance in the cell: \( \rho_{cell} = \rho_{III} > \rho_c, T_1 < T_c \) and the gravitational effect is small. In condition III, the temperature follows to the equality \( T_1 = T_{cross} \). the upper and lower parts have volume, \( V/2 \), and \( \rho_l(T_{cross}) = \rho_g(T_{cross}) \). The level, \( h_l = 0 \), corresponds to the position of the meniscus in the case.

We use the mass balance and record \( \Delta V_g/V \) in condition IV (\( \rho_{cell} = \rho_{III}, T_c > T_2 > T_{cross} \)) in the form

\[
V_g \rho_g + (V - V_g) \rho_l = V \rho_{cell}, \quad \frac{V_g}{V} = \frac{\rho_{cell} - \rho_l}{\rho_g - \rho_l},
\]

(16)
Let us include functions, $\Delta \rho_l$, $\Delta \rho_g$, $\Delta \rho_{\text{cell}} = (\rho_{\text{cell}} - \rho_c)/\rho_c$, in (16) and express $V_g/V$ in the form

$$
\frac{V_g}{V} = \frac{\Delta \rho_l - \Delta \rho_g}{\Delta \rho_l - \Delta \rho_g}.
$$

(17)

It is possible to write down $\Delta \rho_{\text{cell}}$ in condition III as

$$
\Delta \rho_{\text{cell}} = \frac{\Delta \rho_l(T_{\text{cross}}) + \Delta \rho_g(T_{\text{cross}})}{2} = f_d(T_{\text{cross}}).
$$

(18)

We present the displacement, $h_t$, using (11), (17) and (18) in condition IV as

$$
h_t = \pi \frac{d}{8} \left( -ur + \frac{f_d(T_{\text{cross}})}{f_s} \right).
$$

(19)

One can see an additional term, $f_d(T_{\text{cross}})/f_s$, in (19) in comparison with the structure of (12). The term can explain a small difference between ($h_{\text{MV}} = 19.1$ mm) and $d/2 = 20.0$ mm. The displacement $h_t$ (19) has been compared with a similar relation, which is considered in [7]. The equation (19) agrees satisfactorily with the analogous function, $h_{\tau}(\tau) = A(-B(f_d/f_s) + C/f_s)$, which is recommended in [7].

4. Conclusions

Functions $f_s$, $f_d$ (13) and (14) are chosen in scaling forms and built on the base of modified $(\rho_l, \rho_g, T)$ data in the interval $10^{-4} < \tau < 0.2$ for C$_6$F$_6$. Function $f_d$ (13) contains scaling component, $B_{d0}\tau^{2\beta}$, which has $2\beta$ index and $B_{d\text{exp}} > 0$. These features reflect current trends of ST [2–4, 6].

Our analysis has shown that $\rho_l(\tau, D, C)$ and $\rho_g(\tau, D, C)$ represent experimental $\rho_l$, $\rho_g$, $T$ data [1] with an acceptable accuracy in the interval $2 \times 10^{-4} < \tau < 0.2$. Root mean square deviations, $(S_l, S_g)$, of modified $(\rho_l, \rho_g, T)$ data from equations (15) are determined as $S_g = 0.48\%$, $S_l = 0.12\%$. Approximation models $(\rho_l(\tau), \rho_g(\tau))$ [1] do not meet the requirements of ST in the critical region.
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