

EQUATIONS OF CRITICAL VISCOSITY AND LIMITS OF THEIR APPLICATION

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UDC 532.536
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On the basis of available experimental data on the behavior of liquid systems near the critical temperature, we define the limits of application of the equations of critical viscosity which are proposed on the basis of the theory of dynamical scaling. It is shown that the reciprocal value of the wave vector in these equations equals to the correlation length on the boundary of the hydrodynamic region.

According to the theory of dynamical scaling [1–2], the liquid viscosity in the critical region is described by the relation

$$\begin{aligned} \eta(T) &= \eta_r(T) + \eta_f(T) = \eta_r(T)(qR_c)^{z_\eta} = \\ &= \eta_r(T)(r_0q)^{z_\eta} t^{-\nu z_\eta}. \end{aligned} \quad (1)$$

Here, $\eta_r(T) = A \exp \frac{B}{T}$ is the regular part of viscosity which omits the fluctuations of density or concentration in a liquid system; η_f is the fluctuation part of viscosity; $z_\eta = 0.050 \div 0.065$ is the critical viscosity exponent; q is the wave vector [1, 2]; $R_c = r_0 t^{-\nu}$ is the correlation length [3]; $t = (T - T_c)/T_c$, and T_c is the critical temperature.

As seen, the region of application of this relation is bounded. Indeed, according to (1), the liquid viscosity tends to infinity at $t \rightarrow 0$. However, the analysis of all available data indicates that viscosity takes just a finite value at the critical point (CP). Thus, relation (1) is not true near the critical temperature ($t \rightarrow 0$). The specific lower bound for the validity of this formula also is not defined (far from CP).

With regard for the above-presented, the goal of this work is the definition of a specific region of validity of the critical viscosity equation (1). It is clear from (1)

that $\eta/\eta_r = (qR)^{z_\eta} > 1$. Therefore, we may assume that this equation can be used only beyond the limits of the hydrodynamic region $(qR_c) = (qr_0 t^{-\nu}) > 1$. To determine a specific temperature region of the validity of the last relation, ($t < (qr_0)^{1/\nu}$), we need to find a value of the wave vector q which defines, together with the other parameters of (1) [1, 2], the viscosity characteristics of a liquid system near CP.

To this end, we consider firstly the temperature region $t > (qr_0)^{1/\nu}$, where the hydrodynamic approximation $qR_c < 1$ is valid. In order that the viscosity equation (1) be true in this temperature region, the crossover function $F(x) = (1 + Bt^n) > 1$ was introduced in [4], where $Bt^n \ll 1$.

Then the critical viscosity equation (1) takes the form [4]

$$\eta/\eta_r = (qR_c)^{z_\eta} F(x) = (qR_c)^{z_\eta} (1 + Bt^n). \quad (2)$$

Far from CP on the fluctuation region boundary in the case where η/η_r tends to 1, (2) yields the inequality

$$1 \gg (qR) \geq (1 - B/z_\eta t^n). \quad (3)$$

Whence we get that $B/z_\eta t^n \leq 1$.

That is, the temperature region of the validity of Eq. (2) can be determined from the inequality $t^n \leq z_\eta/B$.

To estimate the parameters n and B from the last inequality and (3), we use the fact that, far from CP, the ratio η/η_r tends to the constant value, $\eta/\eta_r = 1$, weakly depending on temperature. Thus, we may assume that the derivative

$$\frac{d}{dt}(\eta/\eta_r \approx 1) = \frac{d}{dt}[(qR_c)^{z_\eta} (1 + Bt^n)] = 0. \quad (4)$$

on the fluctuation region boundary in the case where $\eta/\eta_r = 1$.

Whence we obtain the term of the crossover function $F(x)$ [4] in (2):

$$Bt^n = \frac{\nu z_\eta}{n - \nu z_\eta}. \quad (5)$$

In the case where $n \gg \nu z_\eta \approx 0.03$, (5) is simplified to $Bt^n = \frac{\nu z_\eta}{n}$. By comparing this result with the inequality $t^n \leq z_\eta/B$, we get $n \approx \nu$. That is, the value of the exponent n in (2) is close to that of the critical index of the correlation length, $\nu \approx 2/3$ [3]. This conclusion is really confirmed by the experimental data [5–7] which yield that $n \approx 0.6 \div 0.7$.

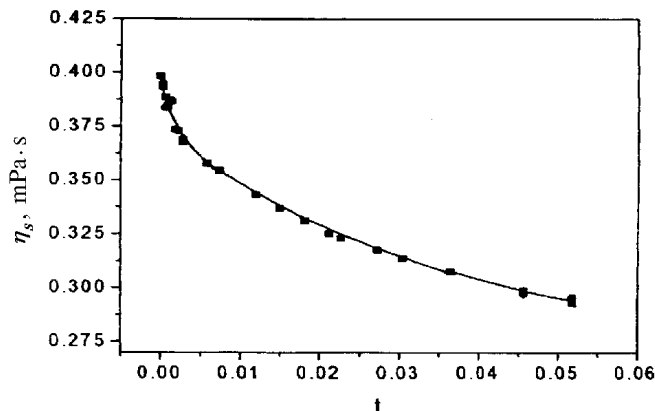
In view of (3), we try below to estimate the value of $B \leq z_\eta t^{-\nu}$ and the reciprocal value of the wave vector $q^{-1} \gg R_c(t) = r_0 t^{-\nu}$. The last inequality yields that q^{-1} exceeds considerably the correlation length of a system on the fluctuation region boundary in the case where $\eta/\eta_r \approx 1$.

To quantitatively calculate the parameters in (2), it is necessary to define the temperature boundary of the fluctuation region. Earlier, it was shown [8] that the gravitation effect begins to reveal itself namely in the fluctuation region of temperatures $t \leq t_f$. For example, the experimental studies of this effect in the vicinity of the consolute critical temperature of binary solutions [9] showed that the boundary of the fluctuation region is defined by the temperatures $|\Delta T| = |T - T_c| \leq 10 \text{ K}$ ($t_f \leq 3 \cdot 10^{-2}$).

In view of this result and by considering that $z_\eta \approx 0.06$ [5, 6] and $n \approx \nu \approx 2/3$ [3], we found $B \geq 0.63$.

This result is confirmed by the experimental data [4] which yield $B \approx 0.7$. That is, this value is close to that of the critical index of the correlation length $B \approx \nu \approx 2/3$. The fact that the above-calculated parameters n and B are close to experimental values [4] testifies to the validity of assumption (4). Now, we estimate also the reciprocal value of the wave vector: $q^{-1} \gg R_c(t = t_f = 3 \cdot 10^{-2}) = r_0 t_f^{-\nu}$. For the correlation length amplitude $r_0 \approx 3 \text{ \AA}$ [10], the correlation length on the fluctuation region boundary reaches $R_c(t_f) \approx 30 \text{ \AA}$. Then the reciprocal values of the wave vector $q^{-1} \gg R_c(t_f)$ attain $q^{-1} \approx 100 \div 200 \text{ \AA}$. These values of q^{-1} correspond to the correlation length of a liquid system at a temperature $t \approx 10^{-3}$. This yields that the reciprocal value of the wave vector q^{-1} in (1) is close to the correlation length in the system *on the hydrodynamic region boundary* ($qR_c \approx 1$). Thus, Eq. (1), where $qR_c > 1$, can be used only in the temperature region $t < 10^{-3}$.

On the basis of the performed calculations, we propose the following equation instead of (2) in the



Dynamic viscosity of the methanol – hexane solution vs reduced temperature at $T > T_c$

hydrodynamic region $R_c q < 1$:

$$\eta/\eta_r = (qr_0)^{z_\eta} t^{-z_\eta \nu} [1 + \nu t^\nu]. \quad (6)$$

Here, the number of fitting parameters is not more than that in (1).

In view of (1) and (6), the lower boundary of the validity of Eq. (1) is defined by the condition $\nu t_1^\nu \ll 1$. In the limits of real errors of the measurement of viscosity (6) near CP [$\delta(\eta/\eta_r) \approx 10^{-2}$], we may assume that also $\nu t_1^\nu \leq 10^{-2}$. Then the lower boundary of the validity of Eq. (1) is defined as $t_1 \leq 10^{-3}$. Indeed, in this case, the product $qR_c(t_1 = 10^{-3}) > 1$, which yields the inequality $\eta/\eta_r > 1$. Thus, the reciprocal value of the wave vector q^{-1} in (1) equals the correlation length of the system on the lower boundary of the validity of Eq. (1).

To determine the upper boundary of the validity of Eq. (1) at $qR_c = qr_0 t_2^{-\nu} \gg 1$, it is necessary that the condition for the viscosity to be finite at CP be satisfied. To this end, we use the equation for the fluctuation part of viscosity which was advanced in [11, 12]:

$$\eta_f = \frac{\Delta \eta_0 t^{-\nu}}{1 + qR_c}. \quad (7)$$

At CP, $\eta_{fc} = \Delta \eta_0 (qr_0)^{-1} = \text{const}$. By substituting (7) in (1), we get the finite maximum value of the parameter $x_m = qR_c$ which satisfies Eq. (1),

$$x_m = (1 + \eta_{fc}/\eta_{rc})^{1/z_\eta}. \quad (8)$$

Here, η_{fc} and η_{rc} are, respectively, the fluctuation and regular parts of viscosity at the very critical point. By using the last relation, we can find the upper boundary of the validity of Eq. (1).

The analysis of many experimental data on the behavior of the viscosity of liquids near CP showed that the maximum value of the ratio $\eta_{fc}/\eta_{rc} \approx 0.2$ [4–7, 11,

12]. This yields that the parameter x_m reaches the values $x = (qR_c) = 15 \div 20$ on the boundary of this region which correspond to the temperatures $t \approx 10^{-4} \div 10^{-5}$.

Thus, based on the performed calculations, we can define the temperature region for a practical application of Eqs. (1), (2), and (6) by using the inequalities:

$$10^{-4} \div 10^{-5} = t_2 < (1) \leq t_1 = 10^{-3},$$

$$10^{-3} = t_2 \leq (2), (6) \leq t_1 = 10^{-2}. \quad (9)$$

We verified the calculations and conclusions by basing on the experimental data on the critical behavior of the viscosity of such solutions as trimethylpyridine — heavy water [7], methanol — hexane [13], and methanol — heptane [14] near the consolute critical temperature. In the figure, we present the dynamical viscosity of the methanol — hexane solution vs temperature. The continuous line shows the approximation of the experimental data on $\eta(t)$ by (6) with the parameters: $A = 0.021$ MPa, $B = 911$ deg, $q_0 r_0 = 0,03$; $z_\eta \nu = 0.035$, $\nu = 0.62$. As seen, in the limits of experimental errors, $\delta\eta/\eta \approx \pm 0.01$ [11], the continuous line describes completely the experimental data on $\eta(t)$ in the temperature interval $t \approx 10^{-1} \div 10^{-4}$, which indicates the rightfulness of the application of Eq. (6).

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Received 07.10.02.

Translated from Ukrainian by V. V. Kukhtin

РІВНЯННЯ КРИТИЧНОЇ В'ЯЗКОСТІ І МЕЖІ ЇХ ЗАСТОСУВАННЯ

О.Д. Альохін

Резюме

На основі існуючих експериментальних даних з в'язкості рідинних систем поблизу критичної температури визначено межі застосування рівнянь критичної в'язкості, виведених на основі теорії динамічного скейлінгу. Показано, що величина оберненого значення хвильового вектора в цих рівняннях дорівнює радіусу кореляції системи на межі гідродинамічної області.