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## **The Probability Methods for the Description of an Equilibrium Thermodynamic State of the Binary Interacting Mixtures**

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### **Abstract**

By the quasi-static approach according to equality of chemical potentials increments for the components of a mixture of dry air and water vapour in accordance with conditions of phase equilibrium the dimensionless one-particle specific entropy of steam mixture has been defined. The single-particle density distribution functions for the components of a mixture with influence of the temperature effect have been determined. The expressions for the probability of observing the molar fraction of components of the mixture has been written, from which the probability density function of investigated quantity has been obtained in the case of not interacting and interacting mixture components. The interaction between the different kinds of the mixture particles has been described by probabilistic methods using two-particle distribution functions. The main methods of construction and calculation of symmetrized or equilibrium two particle distribution functions have been considered. According to the principle of informational entropy maximum and mathematical methods of functional integration, the expressions to determine of the statistical partition function and the equilibrium entropy for an interacting binary non-ideal vapour-air mixture have been written.

**Keywords:** Statistical Thermodynamics, Entropy, Equilibrium State of Gases Mixture, Volume of Information, Probability Distribution, Density of Distribution Function, Continuous Quantity

### **Introduction**

The main purpose of this publication is arising into the context of more general research which describe the equilibrium thermodynamic state of multiphase (component) media with usage of not classical (not canonical) methods of equilibrium statistical mechanic, when information about energy state such system is not full or not sufficient for applying of classical statistical mechanic methods [1-6].

In such case it's necessary to avoid from the commonly used conception of coordinate phase space and interpret the thermodynamic state of the such system with usage of the probabilistic (macroscopic) methods at condition, what the density distribution function is known for investigated extensive (dynamical) physical quantities and the set of averaged (observed) quantities, which in the state of thermodynamic equilibrium, must be equivalent to the experimental measured characteristics of system [2,4,5].

An essence of the demonstrated in this publication of method for finding of the statistical sum of two component water vapor and air mixture consist of in this, that any closed thermodynamic multiphase and multi component system according to the Boltzmann hypothesize (see for example work ,Poincare theorem) with the passage of time follows to the equilibrium state [2]. Then the arbitrary distribution functions for investigated physical quantities is loss the time dependencies and take on the equilibrium form. Corresponding dynamical quantities in such case are stored and transformed into the movement integrals, which is compatible with microscopic description of selected object of investigation.

Because the investigated continuous quantities are defined in the space of the thermodynamic variables only by

probabilistic manner with usage of corresponding functions of density distribution for observed quantities, so the averaged quantities in general case (not isolated system) also depends on the mentioned distribution functions. Then a general task of described statistical method for investigation of the equilibrium state of a thermodynamic system is founding of an equilibrium distribution of physical quantities which can be resolved analytically only with usage of the mathematical methods of functional integration.

From a point of view of the physical interpretation of investigated equilibrium process a principle of maximum of informational entropy for stochastic system defined by the Shannon is used, according to which the statistical sum of the thermodynamic system may be delivered [4-7]. Mathematically it's represented by the problem of searching extreme of Boltzmann-Lagrange-Shannon functional in the case of the fullness conditions and coincidence of theoretically calculated averaged values of physical quantities (extensive thermodynamic variables) with experimentally measured [1,6].

In this paper the methodology of investigation on the example of the closed two component interaction system (mixture of water vapor and dry air) is described, when question about definition and finding of the averaged quantities is not principled. In such case the statistical sum of system (an extreme of Boltzmann-Lagrange-Shannon functional) is founded only under satisfy the conditions of completeness for the mentioned functions of density distribution, and averaged quantities of mixture temperature and partial pressures of components are taken constant and equal to equilibrium values into all interval of observed values of the molar fraction of mixture component [6].

### The Mathematical Probability of Two Interconnected Events. The Density of Probability or the Function of Distribution Density. Completeness Condition

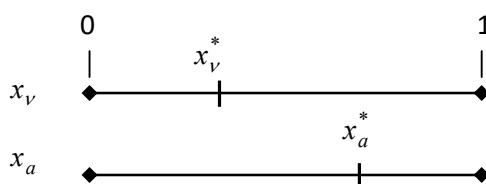


Figure 1: Schematically Depiction of Interconnected  $x_v^*$  and  $x_a^*$  Events

Let's review of continuous mathematical probability for event  $P(x_v^*)$  and  $P(x_a^*)$  what two equivalents for content continuous physical quantities  $x_v$  and  $x_a$  takes the fixed values  $x_{\sigma}^*$ ,  $\sigma = \{v, a\}$  (Figure 1) from the constant interval  $\delta = [0, 1]$  of possible or observed values  $x_{\sigma}$  ( $0 \leq x_{\sigma} \leq 1$ ) under condition, what quantities are interconnected among our serve through relation  $x_v + x_a = 1$  in the form of preservation law.

In the case, then corresponding density distribution functions are known for the probabilities of represented quantities have relations [1].

$$P(x_{\sigma}^*) = \int_0^{x_{\sigma}^*} f_{x_{\sigma}}(\xi) d\xi = \int_{1-x_{\sigma}^*}^1 f_{x_{\sigma}}(1-\eta) d\eta, \quad (1)$$

here  $f_{x_{\sigma}}(\xi)$ , where  $\sigma = \{a, v\}$  is the density of probability or distribution density function for the continuous quantity  $x_{\sigma}$ .

Following from an equation (1) and condition of interconnection ( $x_v + x_a = 1$ ) may also define the probability of inverse events

$$\bar{P}(x) = \int_0^x f(\xi) d\xi \quad \bar{\bar{P}}(x) = \bar{P}(1-x) = \int_0^{1-x} f(\xi) d\xi \quad (x \in \delta), \quad (2)$$

where  $f(\xi)$  is the arbitrary distribution function.

When  $f = f_{x_v}$  we have  $\bar{P}(x) \equiv \{x = x_v^*, P(x_v^*) | x = x_a^*, P(x_a^*)\}$  and the vice versa, if  $f = f_{x_a}$  we get  $\bar{\bar{P}}(x) \equiv \{x = x_v^*, P(x_a^*) | x = x_a^*, P(x_v^*)\}$ . Especially <sup>1</sup>

$$\bar{P}_{x_{\sigma}}(x^*) = \int_0^{x^*} f_{x_{\sigma}}(\xi) d\xi \quad \bar{\bar{P}}_{x_{\sigma}}(x^*) = \bar{P}_{x_{\sigma}}(1-x^*) = \int_0^{1-x^*} f_{x_{\sigma}}(\xi) d\xi \quad (3)$$

where  $\bar{P}_{x_{\sigma}}(x^*)$  and  $\bar{\bar{P}}_{x_{\sigma}}(x^*)$ ,  $\sigma = \{v, a\}$  is the indexed according to selection of distribution function  $f_{x_{\sigma}}(\xi)$  of probability for straight and opposite event under observation of the continuous quantity  $x^*$ .

It should be noted, what defined according to relation (1) probabilities  $P(x_v^*)$  and  $P(x_a^*)$  do not satisfy the fullness condition ( $P(x_v^*) + P(x_a^*) \neq 1$ ). The probabilities of opposite events (2) form a complete group only in the case,

when  $f(\xi) = f(1 - \xi)$ , here  $\xi \in \bar{\delta}$ , where  $\bar{\delta} = [0, 1]$  is the observation interval.

From this it follows, that fullness condition according to (3) advisable to write in the following view

$$\frac{1}{N[f_{x_\sigma}]} \left( \int_0^{x^*} f_{x_\sigma}(\xi) d\xi + \int_0^{1-x^*} f_{x_\sigma}(1-\eta) d\eta \right) = 1 \quad (4)$$

because  $\int_0^{1-x^*} f_{x_\sigma}(1-\eta) d\eta = \int_{x^*}^1 f_{x_\sigma}(\xi) d\xi$ , and  $N[f_{x_\sigma}] = \int_0^1 f_{x_\sigma}(\xi) d\xi = \int_0^1 f_{x_\sigma}(1-\eta) d\eta$  is

the norm of corresponding distribution function<sup>2</sup>.

### The Two-Component Water Vapour and Dry Air Mixture, Chemical Potential and One-Particle Distribution Function. Consideration of the Temperature Effects

For starters let's define the two-component gas mixture as a thermodynamic object which consists from two molecular non-interacting subsystems  $\Xi_v$  and  $\Xi_a$  ( $\sigma = \{v, a\}$ , where v and a are the components of water vapor and dry air correspondingly), which can be characterized by the set of individual intensive ( $T_\sigma$  is the thermodynamic temperature,  $p_\sigma$  is the partial pressure) and extensive ( $x_\sigma$  is the molar fraction of mixture components) quantities.

According to the work the chemical potential of one mole of  $\sigma$ -component of gas mixture has the following view [8].

$$\mu_\sigma(T_\sigma, p_\sigma; x_\sigma) = \mu_\sigma^0(T_\sigma, p_\sigma) + \frac{RT_\sigma}{M_\sigma} \ln[x_\sigma], \quad (5)$$

here  $\mu_\sigma^0(T_\sigma, p_\sigma)$  is the chemical potential of non-interaction component.

Taking the differential from the chemical potential (5), we get

$$d\mu_\sigma(T_\sigma, p_\sigma; x_\sigma) = d\mu_\sigma^0(T_\sigma, p_\sigma) + \frac{RT_\sigma}{M_\sigma} \frac{dx_\sigma}{x_\sigma} + \frac{R}{M_\sigma} \ln[x_\sigma] dT_\sigma + \frac{RT_\sigma}{M_\sigma} \frac{dp_\sigma}{p_\sigma} \quad (6)$$

here  $d\mu_\sigma^0(T_\sigma, p_\sigma) = -s_\sigma^0(T_\sigma, p_\sigma) dT_\sigma + (1/\rho_\sigma) dp_\sigma$  is the differential of chemical

potential for selected component,  $s_\sigma^0(T_\sigma, p_\sigma)$  is the specific mass entropy,  $\rho_\sigma = \frac{M_\sigma p_\sigma}{RT_\sigma}$  is the partial density,  $M_\sigma$  is the molar mass and R is the universal gas constant [8].

It is known what in the state of thermodynamic equilibrium at interaction of subsystems  $\Xi_v$  and  $\Xi_a$ : [9]. The temperature of gas mixture components is aligned  $T_v = T_a = T$  (this is the principle of local thermal equilibrium); 2. The partial pressures of mixture components are tending to equal value  $p_v = p_a = \langle p \rangle$ . Under different conditions, as a rule  $p_\sigma = f(T, \langle p \rangle; x_v)$ , where f is the function, which can be determined according to equation of state.

In the case of ideal mixing of mixture components, when the law of mass conservation for the amount of substance  $x_v + x_a = 1$  is satisfied, we have [10].

$$\mu_{mix} = \sum_\sigma x_\sigma \mu_\sigma(T, p_\sigma; x_\sigma), \quad (7)$$

from which it is received

$$d\mu_{mix} = \sum_\sigma x_\sigma d\mu_\sigma(T, p_\sigma; x_\sigma) + \sum_\sigma \mu_\sigma(T, p_\sigma; x_\sigma) dx_\sigma \quad (8)$$

At the conditions of phase equilibrium [9]. We have  $\sum_\sigma \mu_\sigma^0(T_\sigma, p_\sigma) dx_\sigma = 0$ , so into expression (8)  $\sum_\sigma \mu_\sigma(T, p_\sigma; x_\sigma) dx_\sigma = RT \sum_\sigma \frac{1}{M_\sigma} \ln[x_\sigma] dx_\sigma$ . Then according to previous meaning, if through  $\bar{x} = \{x_v, x_a\}$  can be defined the sets of values for molar fraction of mixture components, we have received

$$d\mu_{mix}(T, p_\sigma; \bar{x}) = \sum_\sigma x_\sigma d\mu_\sigma^0(T_\sigma, p_\sigma) + RT \left\{ \left[ \sum_\sigma \frac{x_\sigma}{M_\sigma} \ln[x_\sigma] \right] \frac{dT}{T} + \sum_\sigma \left[ \frac{1}{M_\sigma} (1 + \ln[x_\sigma]) \right] dx_\sigma \right\}$$

Let's define the dimensionless chemical potential  $\tilde{\mu}_{mix}$  through relation

$$d\mu_{mix}(T, p_\sigma; \bar{x}) = \frac{RT}{\langle M \rangle} d\tilde{\mu}_{mix}(T, p_\sigma; \bar{x}) = \frac{kT}{\langle n \rangle} d\tilde{\mu}_{mix}(T, p_\sigma; \bar{x}) \quad (9)$$

where  $\langle M \rangle = M_v M_a / (M_v + M_a)$  is the averaged molar mass of mixture,  $\langle n \rangle = \langle M \rangle / N_A$  is the average number of particles per unit mass of mixture,  $R = k N_A$  is the universal gas constant,  $k$  is the Boltzmann constant and  $N_A$  is the Avogadro's number.

So in the state of thermodynamic equilibrium ( $p_v = p_a = \langle p \rangle$ ) under ideal mixing of mixture components we received

$$d\tilde{\mu}_{mix}(T, p_\sigma; \bar{x}) = - \left[ \sum_{\sigma} x_{\sigma} \tilde{s}_{\sigma}^0(T, \langle p \rangle) \right] \frac{dT}{T} + \frac{d\langle p \rangle}{\langle p \rangle} + RT \left\{ \left[ \sum_{\sigma} \frac{\langle M \rangle}{M_{\sigma}} x_{\sigma} \text{Ln}[x_{\sigma}] \right] \frac{dT}{T} + \sum_{\sigma} \left[ \frac{\langle M \rangle}{M_{\sigma}} (1 + \text{Ln}[x_{\sigma}]) \right] dx_{\sigma} \right\} \quad (10)$$

where  $\tilde{s}_{\sigma}^0(T, \langle p \rangle) = s_{\sigma}^0(T, \langle p \rangle) / kN_A$  is dimensionless specific entropy of component,  $p$  is the equilibrium value of partial pressure.

From the expressions (9) and (10) it follows, that dimensionless one-particle  $\tilde{s}_{mix}^0$  entropy of mixture takes the view

$$\tilde{s}_{mix}^0(T, \langle p \rangle; \bar{x}) = \frac{1}{\langle n \rangle} \tilde{s}_{mix}^0(T, \langle p \rangle; \bar{x}) = \frac{1}{\langle n \rangle} \sum_{\sigma} x_{\sigma} \tilde{s}_{\sigma}^0(T, \langle p \rangle) \quad (11)$$

where  $\tilde{s}_{mix}^0(T, \langle p \rangle; \bar{x}) = \sum_{\sigma} x_{\sigma} \tilde{s}_{\sigma}^0(T, \langle p \rangle)$  is the dimensionless specific entropy of mixture.

As usual, the nature of the real two component mixture is far from the simple mixing law (7) and (11) for non-interacting components due to the complex character of inter particle interaction. In such case, the most real is the description of such two component system with usage of the probability methods of statistical physic. It turns out that with applying of such methods it is possibility to gets the analytical expression for entropy (11), which considering interaction between components of mixture [4,5].

On this occasion, according to the expression (10) let's define a one particle distribution function for the components of the mixture

$$f_{x_v}(\xi, T) = \text{Exp} \left( \alpha(T) \frac{\langle M \rangle}{M_v} \xi \text{Ln}[\xi] \right) \quad f_{x_a}(\eta, T) = \text{Exp} \left( -\beta(T) \frac{\langle M \rangle}{M_a} \eta \text{Ln}[\eta] \right) \quad (12)$$

here  $\alpha(T) = \text{Ln}[T/T_{cr2}] + 1$  та  $\beta(T) = \text{Ln}[T/T_{cr2}] - 1$  is the temperature correction to distribution function,  $T = T_{cr1} + t(T_{cr2} - T_{cr1})$  - is the thermodynamic temperature,  $T_{cr1}$  and  $T_{cr2}$  are the corresponding critical values (the points of crystallization and boiling of water),  $t$  is the dimensionless temperature parameter.

It is needing to remarks that for product of such the different varieties distribution functions the properties is satisfied

$$f(x) \equiv f_{x_v}(x, T) f_{x_a}(x, T) = \text{Exp}(x \text{Ln}[x]) \quad (13)$$

In the simplest ideal case interacting components under condition  $x_v + x_a = 1$  we have

$$d\tilde{s}_{mix}^0(T, x) = \frac{1}{2} \sum_{\sigma} [d\sigma_{x_{\sigma}}(T, x_{\sigma}) + d\sigma_{x_{\sigma}}(T, 1 - x_{\sigma})],$$

Where  $d\sigma_{x_{\sigma}}(T, x_{\sigma}) = -df_{x_{\sigma}}(x_{\sigma}, T) / f_{x_{\sigma}}(x_{\sigma}, T)$ ,  $\sigma = \{v, a\}$  is dimensionless information entropy defined by

Shannon ( $\sigma_{x_{\sigma}}(T, x_{\sigma}) = -\text{Ln}[f_{x_{\sigma}}(x_{\sigma}, T)]$ ) [7]. Than

$$\begin{aligned} d\tilde{s}_{mix}^0(T, x) &= -\frac{\langle M \rangle}{M_{eff}^{(-)}(x)} \frac{dT}{T} - d \left[ \frac{\langle M \rangle}{M_{eff}^{(+)}(x)} \right] = \\ &= -\frac{\langle M \rangle}{M_{eff}^{(-)}(x)} \frac{dT}{T} + \left\{ \frac{\langle M \rangle}{M_v} (1 + \text{Ln}[x]) - \frac{\langle M \rangle}{M_a} (1 + \text{Ln}[1 - x]) \right\} dx \end{aligned}$$

here  $M_{eff}^{(\pm)}(x) = -1 / \left\{ \frac{1}{M_v} x \text{Ln}[x] \pm \frac{1}{M_a} (1 - x) \text{Ln}[1 - x] \right\}$  is defined in a clear mathematical form effective molar mass.

The main goal of this paper is receiving an expression and calculation of entropy of interacting two component mixture with usage of pointed distribution functions<sup>3</sup>.

### Non Interacting Components of Mixture. Two Particle Distribution Function for One Sorter Particles

The primary probabilistic description of the non-interacting components of water vapour-air mixture may be realized on the base of the relation (3) and condition (4) of normalization. For which (see Section 1-2 with reference) the probability of inverse events for components of mixture can be introduced [8,9].

$$\tilde{P}_{x_v}^{(1)}(x) = 1 - \frac{1}{N[f_{x_a}^t]} \bar{P}_{x_a}(x), \quad \tilde{P}_{x_v}^{(2)}(x) = 1 - \frac{1}{N[f_{x_a}^t]} \bar{P}_{x_a}(x),$$

$$\tilde{P}_{x_a}^{(1)}(x) = 1 - \frac{1}{N[f_{x_v}^t]} \bar{P}_{x_v}(x), \quad \tilde{P}_{x_a}^{(2)}(x) = 1 - \frac{1}{N[f_{x_v}^t]} \bar{P}_{x_v}(x),$$

here  $N[f_{x_\sigma}^t] = \iint_{\bar{\delta}=[0,1]} f_{x_\sigma}^t(\xi, t) d\xi dt \equiv \iint_{\bar{\delta}=[0,1]} f_{x_\sigma}^t(\xi) d\xi dt$ , where  $\sigma = \{v, a\}$  is the norm of one

particle distribution function (12), when integration is applied through molar fraction of the component and thermodynamic temperature of the mixture.

here  $N[f_{x_\sigma}^t] = \iint_{\bar{\delta}=[0,1]} f_{x_\sigma}^t(\xi, t) d\xi dt \equiv \iint_{\bar{\delta}=[0,1]} f_{x_\sigma}^t(\xi) d\xi dt$ , where  $\sigma = \{v, a\}$  is the norm of one

particle distribution function (12), when integration is applied through molar fraction of the component and thermodynamic temperature of the mixture.

Then under ideal mixing of the mixture components without considering of interaction according to known (12) distribution function  $f_{x_v}^t(x)$  for averaged values of probabilities for observation of water vapour  $\langle P_{x_v}^{(+)}(x) \rangle$  and dry air  $\langle P_{x_v}^{(-)}(x) \rangle$  we have

$$\langle P_{x_v}^{(+)}(x) \rangle = \frac{1}{2} \left\{ 1 + \frac{1}{N[f_{x_v}^t]} [\bar{P}_{x_v}(x) - \bar{P}_{x_v}(x)] \right\} = \frac{1}{2} (\bar{P}_{x_v}^N(x) + \tilde{P}_{x_a}^{(1)}(x))$$

$$\langle P_{x_v}^{(-)}(x) \rangle = \frac{1}{2} \left\{ 1 - \frac{1}{N[f_{x_v}^t]} [\bar{P}_{x_v}(x) - \bar{P}_{x_v}(x)] \right\} = \frac{1}{2} (\bar{P}_{x_v}^{\bar{N}}(x) + \tilde{P}_{x_a}^{(2)}(x))$$
(14)

here  $\bar{P}_{x_v}^N(x) = \frac{1}{N[f_{x_v}^t]} \int_0^x f_{x_v}^t(\xi) d\xi$  та  $\bar{P}_{x_v}^{\bar{N}}(x) = \frac{1}{N[f_{x_v}^t]} \int_x^1 f_{x_v}^t(1-\eta) d\eta$  is the normalized

probability of direct and inverse events for v - function of distribution.

Also, it is possible to write the analogous relations for averaged probabilities of observation for dry air  $\langle P_{x_a}^{(+)}(x) \rangle$  and water vapour  $\langle P_{x_a}^{(-)}(x) \rangle$  on the base of distribution function  $f_{x_a}^t(x)$  (12) as the following

$$\langle P_{x_a}^{(+)}(x) \rangle = \frac{1}{2} \left\{ 1 + \frac{1}{N[f_{x_a}^t]} [\bar{P}_{x_a}(x) - \bar{P}_{x_a}(x)] \right\} = \frac{1}{2} (\bar{P}_{x_a}^N(x) + \tilde{P}_{x_v}^{(1)}(x))$$

$$\langle P_{x_a}^{(-)}(x) \rangle = \frac{1}{2} \left\{ 1 - \frac{1}{N[f_{x_a}^t]} [\bar{P}_{x_a}(x) - \bar{P}_{x_a}(x)] \right\} = \frac{1}{2} (\bar{P}_{x_a}^{\bar{N}}(x) + \tilde{P}_{x_v}^{(2)}(x))$$
, (15)

here  $\bar{P}_{x_a}^N(x) = \frac{1}{N[f_{x_a}^t]} \int_0^x f_{x_a}^t(\xi) d\xi$  та  $\bar{P}_{x_a}^{\bar{N}}(x) = \frac{1}{N[f_{x_a}^t]} \int_x^1 f_{x_a}^t(1-\eta) d\eta$  is the

normalized probability of direct and reverse events for a - function of distribution.

From these relations (14) and (15) it is follows that for defined probabilities the boundary conditions are going

$$\langle P_{x_v}^{(+)}(0) \rangle = \langle P_{x_v}^{(-)}(1) \rangle = 0 \quad \langle P_{x_v}^{(+)}(1) \rangle = \langle P_{x_v}^{(-)}(0) \rangle = 1$$

$$\langle P_{x_a}^{(+)}(0) \rangle = \langle P_{x_a}^{(-)}(1) \rangle = 0 \quad \langle P_{x_a}^{(+)}(1) \rangle = \langle P_{x_a}^{(-)}(0) \rangle = 1$$
(16)

and automatically the fulfil conditions are satisfied

$$\langle P_{x_v}^{(+)}(x) \rangle + \langle P_{x_v}^{(-)}(x) \rangle = 1 \quad \langle P_{x_a}^{(+)}(x) \rangle + \langle P_{x_a}^{(-)}(x) \rangle = 1,$$

Because the analytical expressions for (14) and (15) is taking the view

$$\langle P_{x_\sigma}^{(+)}(x) \rangle = \frac{1}{2} \left( 1 + \frac{1}{N[f_{x_\sigma}^t]} \int_{x-1/2}^{1/2-x} f_{x_\sigma}^t (1/2 + \eta) d\eta \right)$$

$$\langle P_{x_\sigma}^{(-)}(x) \rangle = \frac{1}{2} \left( 1 + \frac{1}{N[f_{x_\sigma}^t]} \int_{1/2-x}^{x-1/2} f_{x_\sigma}^t (1/2 - \xi) d\xi \right)$$

where  $\sigma = \{v, a\}$  is the index, which corresponds to a component of the mixture.

The probability density or distribution function for non-interacting components of a mixture

$$g_{x_v}^{(\pm)}(x) = \frac{d\langle P_{x_v}^{(\pm)}(x) \rangle}{dx} = -\frac{1}{2} \frac{1}{N[f_{x_v}^t]} [f_{x_v}^t(x) + f_{x_v}^t(1-x)]$$

$$g_{x_a}^{(\pm)}(x) = \frac{d\langle P_{x_a}^{(\pm)}(x) \rangle}{dx} = \frac{1}{2} \frac{1}{N[f_{x_a}^t]} [f_{x_a}^t(x) + f_{x_a}^t(1-x)]$$
(17)

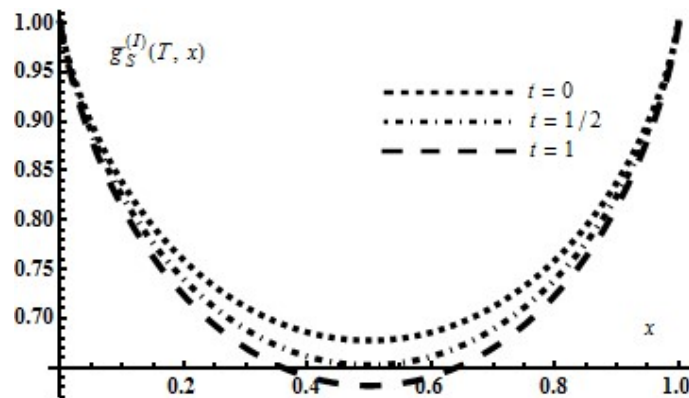
The summarized function of two particles and one sort distribution takes the form [2].

$$g_S^{(I)}(T, x) = g_{x_v}^{(+)}(x)g_{x_v}^{(-)}(1-x) = g_{x_a}^{(+)}(1-x)g_{x_a}^{(-)}(x). \quad (18)$$

With considering of boundary conditions (16) we follow to not normalized right view for pointed distribution function

$$\bar{g}_S^{(I)}(T, x) = 1 - g_{x_v}^{(+)}(x)g_{x_v}^{(-)}(1-x) + g_{x_v}^{(+)}(0)g_{x_v}^{(-)}(1) =$$

$$= 1 - g_{x_a}^{(+)}(1-x)g_{x_a}^{(-)}(x) + g_{x_a}^{(+)}(1)g_{x_a}^{(-)}(0) \quad (19)$$



**Figure 2: Two Particle not Normalized Distribution Function  $\bar{g}_S^{(I)}(T, x)$  into Approach Non-Interacting One Sort Components of Mixture**

Such function of distribution under different values of temperature (this is dimensionless parameter  $t$ ) is depicted on the Figure.2 into the form of one minimal symmetrical curve4.

### Accounting of Interaction Between Components of Mixture. The Two Particle Function of Two Sort Distribution of the Component Mixture

Interaction between of mixture component for water vapour and dry air mixture we describe according to relation (12) with helping of the product  $f(x) = f_{x_v}(x) f_{x_a}(x)$  (13) of two one particle different sort distribution.

In such case correspondingly the averaged probability of observation for continuous quantity  $x$  into two components not interacting mixture we can represent into expressions

$$\langle P_L^{(+)}(x) \rangle = \frac{1}{2} \left( 1 + \frac{1}{N[f_{x_v}^t]} \int_0^x f_{x_v}^t(\xi) d\xi - \frac{1}{N[f_{x_a}^t]} \int_x^1 f_{x_a}^t(1-\eta) d\eta \right)$$

$$\langle P_R^{(+)}(x) \rangle = \frac{1}{2} \left( 1 + \frac{1}{N[f_{x_a}^t]} \int_0^x f_{x_a}^t(\xi) d\xi - \frac{1}{N[f_{x_v}^t]} \int_x^1 f_{x_v}^t(1-\eta) d\eta \right)$$
(20)

and

$$\langle P_L^{(-)}(x) \rangle = 1 - \langle P_L^{(+)}(x) \rangle \quad \langle P_R^{(-)}(x) \rangle = 1 - \langle P_R^{(+)}(x) \rangle. \quad (21)$$

Let's remark that, analogically to relation (16) previous subsection, for the given probabilities (20) and (21) automatically the boundary conditions are satisfied

$$\langle P_{\alpha}^{(+)}(0) \rangle = \langle P_{\alpha}^{(-)}(1) \rangle = 0 \quad \langle P_{\alpha}^{(+)}(1) \rangle = \langle P_{\alpha}^{(-)}(0) \rangle = 1, \quad \alpha = \{L, R\}. \quad (22)$$

The probability properties of interacting two component mixture we are found into the form

$$P_{L1}^{(+)}(x) = \langle P_L^{(+)}(x) \rangle + \frac{1}{2} \bar{\alpha}_1^{(+)}(x) \frac{1}{N[f]} \int_0^{1/2-x} f(1/2 - \xi) d\xi$$

$$P_{L2}^{(-)}(x) = \langle P_L^{(-)}(x) \rangle - \frac{1}{2} \bar{\beta}_1^{(-)}(x) \frac{1}{N[f]} \int_{x-1/2}^0 f(1/2 - \xi) d\xi \quad (23)$$

and

$$P_{R1}^{(+)}(x) = \langle P_R^{(+)}(x) \rangle + \frac{1}{2} \bar{\beta}_1^{(+)}(x) \frac{1}{N[f]} \int_0^{1/2-x} f(1/2 + \eta) d\eta$$

$$P_{R2}^{(-)}(x) = \langle P_R^{(-)}(x) \rangle - \frac{1}{2} \bar{\alpha}_2^{(-)}(x) \frac{1}{N[f]} \int_{x-1/2}^0 f(1/2 + \eta) d\eta \quad (24)$$

where  $\bar{\alpha}_k^{(\pm)}(x)$  and  $\bar{\beta}_k^{(\mp)}(x)$ ,  $k=\{1,2\}$  are functions, with it is necessary to evaluate.

The boundary conditions for probabilities  $P_{Lk}^{(\pm)}(x)$  and  $P_{Rk}^{(\pm)}(x)$ , where  $k=\{1,2\}$  we are represented into the following form

$$P_{L1}^{(+)}(0) = P_{L2}^{(-)}(1) = 1/2 \quad P_{L1}^{(+)}(1) = P_{L2}^{(-)}(0) = 1/2$$

$$P_{R1}^{(+)}(0) = P_{R2}^{(-)}(1) = 1/2 \quad P_{R1}^{(+)}(1) = P_{R2}^{(-)}(0) = 1/2 \quad (25)$$

Then the fullness conditions according to (22) under arbitrary values of investigated continuous quantity must be satisfied without any warnings

$$P_{L1}^{(+)}(x) + P_{L2}^{(-)}(x) = 1 \quad P_{R1}^{(+)}(x) + P_{R2}^{(-)}(x) = 1. \quad (26)$$

If introduce the denotation

$$F_{\alpha 1}^{(L)}(x) = \frac{1}{N[f]} \int_0^{1/2-x} f(1/2 - \xi) d\xi \quad F_{\beta 1}^{(L)}(x) = \frac{1}{N[f]} \int_{x-1/2}^0 f(1/2 - \xi) d\xi$$

$$F_{\beta 2}^{(R)}(x) = \frac{1}{N[f]} \int_0^{1/2-x} f(1/2 + \eta) d\eta \quad F_{\alpha 2}^{(R)}(x) = \frac{1}{N[f]} \int_{x-1/2}^0 f(1/2 + \eta) d\eta \quad (27)$$

Then the fullness conditions (26) takes the view of system of equations for unknown functions  $\bar{\alpha}_k^{(\pm)}(x)$  and  $\bar{\beta}_k^{(\pm)}(x)$ , here  $k=\{1,2\}$ , which subject to determination

$$\begin{cases} \frac{1}{2} (1 + \bar{\alpha}_1^{(+)}(x) F_{\alpha 1}^{(L)}(x)) + \frac{1}{2} (1 - \bar{\beta}_1^{(-)}(x) F_{\beta 1}^{(L)}(x)) = 1 \\ \frac{1}{2} (1 + \bar{\beta}_2^{(+)}(x) F_{\beta 2}^{(R)}(x)) + \frac{1}{2} (1 - \bar{\alpha}_2^{(-)}(x) F_{\alpha 2}^{(R)}(x)) = 1 \end{cases} \quad (28)$$

Applying the boundary conditions (25) for the searching functions in the relations (23) and (24) on the edges of the interval  $\delta = [0,1]$  of possible argument values, we gets

$$\bar{\alpha}_1^{(+)}(0) = \bar{\beta}_1^{(-)}(1) = 1 / F_{\alpha 1}^{(L)}(0) \quad \bar{\alpha}_1^{(+)}(1) = \bar{\beta}_1^{(-)}(0) = 1 / F_{\beta 1}^{(L)}(0)$$

$$\bar{\alpha}_2^{(-)}(1) = \bar{\beta}_2^{(+)}(0) = 1 / F_{\beta 2}^{(R)}(0) \quad \bar{\alpha}_1^{(-)}(0) = \bar{\beta}_1^{(+)}(1) = 1 / F_{\alpha 2}^{(R)}(0) \quad (29)$$

By the way of differentiation the system of (28) we reduce to the form

$$\begin{cases} \frac{1}{2} \bar{\alpha}_1^{(+)}(x) F_{\alpha 1}^{(L)}(x) \delta \varphi_{\alpha 1}^{(L)}(x) - \frac{1}{2} \bar{\beta}_1^{(-)}(x) F_{\beta 1}^{(L)}(x) \delta \psi_{\beta 1}^{(L)}(x) = 0 \\ \frac{1}{2} \bar{\beta}_2^{(+)}(x) F_{\beta 2}^{(R)}(x) \delta \psi_{\beta 2}^{(R)}(x) - \frac{1}{2} \bar{\alpha}_2^{(-)}(x) F_{\alpha 2}^{(R)}(x) \delta \varphi_{\alpha 2}^{(R)}(x) = 0 \end{cases} \quad (30)$$

where

$$\delta \varphi_{\alpha k}^{(\lambda)}(x) = \frac{1}{\bar{\alpha}_k^{(\pm)}(x)} \frac{d\bar{\alpha}_k^{(\pm)}(x)}{dx} + \frac{1}{F_{\alpha k}^{(\lambda)}(x)} \frac{dF_{\alpha k}^{(\lambda)}(x)}{dx}$$

$$\delta \psi_{\beta k}^{(\lambda)}(x) = \frac{1}{\bar{\beta}_k^{(\mp)}(x)} \frac{d\bar{\beta}_k^{(\mp)}(x)}{dx} + \frac{1}{F_{\beta k}^{(\lambda)}(x)} \frac{dF_{\beta k}^{(\lambda)}(x)}{dx}$$

are corresponds to indexes  $k=\{1,2\}$  and  $\lambda=\{L, R\}$  into differential forms of first order, in which the selection of the sign into internal area of expression take a place according to the mentioned above indexes by the rules

$$\delta\varphi_{\alpha k}^{(\lambda)} \rightarrow \begin{cases} k=1 \cup \lambda=L, "+" \\ k=2 \cup \lambda=R, "-" \end{cases} \quad \delta\psi_{\beta k}^{(\lambda)} \rightarrow \begin{cases} k=1 \cup \lambda=L, "-" \\ k=2 \cup \lambda=R, "+" \end{cases}$$

The unknown functions  $\bar{\alpha}_k^{(\pm)}(x)$  and  $\bar{\beta}_k^{(\mp)}(x)$ , as the general solving of the system of first order homogeneous differential equations (30), we found on the base of partial solution of four differential equations

$$\delta\varphi_{\alpha k}^{(\lambda)}(x)=0 \quad \delta\psi_{\beta k}^{(\lambda)}(x)=0,$$

which takes the form  $\bar{\alpha}_k^{(\pm)}(x) = A_k^{(\lambda)}(x) / F_{\alpha k}^{(\lambda)}(x)$  and  $\bar{\beta}_k^{(\mp)}(x) = B_k^{(\lambda)}(x) / F_{\beta k}^{(\lambda)}(x)$ , where

$A_k^{(\lambda)}(x) = g_{\alpha}^{(\lambda)} F_{\alpha k}^{(\lambda)}(x) + g_{\beta}^{(\lambda)} F_{\beta k}^{(\lambda)}(x)$  and  $B_k^{(\lambda)}(x) = g_{\alpha}^{(\lambda)} F_{\alpha k}^{(\lambda)}(x) + g_{\beta}^{(\lambda)} F_{\beta k}^{(\lambda)}(x)$  and are the lineal combination of known integrals (27) for light definition ( $g_{\alpha}^{(\lambda)} = g_{\beta}^{(\lambda)} = 1$ ) according to boundary conditions (29), here  $g_{\alpha}^{(\lambda)}$  and  $g_{\beta}^{(\lambda)}$  are sought constants.

So we receive the solution of equivalents system of equations (28) and (30), which satisfy the boundary conditions (29) in the form

$$\begin{aligned} \bar{\alpha}_1^{(+)}(x) &= 1 + F_{\beta 1}^{(L)}(x) / F_{\alpha 1}^{(L)}(x) & \bar{\beta}_1^{(-)}(x) &= 1 + F_{\alpha 1}^{(L)}(x) / F_{\beta 1}^{(L)}(x) \\ \bar{\beta}_2^{(+)}(x) &= 1 + F_{\alpha 2}^{(R)}(x) / F_{\beta 2}^{(R)}(x) & \bar{\alpha}_2^{(-)}(x) &= 1 + F_{\beta 2}^{(R)}(x) / F_{\alpha 2}^{(R)}(x) \end{aligned} \quad (31)$$

The probability density or distribution functions for interacting particles of mixture components we receive by the differentiation of corresponding (23) and (24) with considering the mentioned above solution (31) of the system equations as

$$\begin{aligned} g_{L1}^{(+)}(x) &= dP_{L1}^{(+)}(x) / dx & g_{L2}^{(-)}(x) &= dP_{L2}^{(-)}(x) / dx \\ g_{R1}^{(+)}(x) &= dP_{R1}^{(+)}(x) / dx & g_{R2}^{(-)}(x) &= dP_{R2}^{(-)}(x) / dx \end{aligned}$$

In the final case we gets

$$\begin{aligned} g_{L1}^{(+)}(x) &= \frac{1}{2} \left( \frac{f_{x_v}^t(x)}{N[f_{x_v}^t]} + \frac{f_{x_a}^t(1-x)}{N[f_{x_a}^t]} \right) - \frac{1}{2} \frac{1}{N[f]} (f(x) + f(1-x)) \\ g_{R1}^{(+)}(x) &= \frac{1}{2} \left( \frac{f_{x_a}^t(x)}{N[f_{x_a}^t]} + \frac{f_{x_v}^t(1-x)}{N[f_{x_v}^t]} \right) - \frac{1}{2} \frac{1}{N[f]} (f(x) + f(1-x)) \end{aligned} \quad (32)$$

where  $g_{L2}^{(-)}(x) = -g_{L1}^{(+)}(x)$  та  $g_{R2}^{(-)}(x) = -g_{R1}^{(+)}(x)$  is opposite or reverse distributions.

When the symmetrized function of two particles distribution the two different types or sorts has the following view [2].

$$g_S^{(II)}(T, x) = g_{L1}^{(+)}(x)g_{L2}^{(-)}(1-x) = g_{R1}^{(+)}(1-x)g_{R2}^{(-)}(x) \quad (33)$$

With considering boundary conditions (22) we're going to not normalized view for mentioned distribution function

$$\begin{aligned} \bar{g}_S^{(II)}(T, x) &= 1 - g_{L1}^{(+)}(x)g_{L2}^{(-)}(1-x) + g_{L1}^{(+)}(0)g_{L2}^{(-)}(1) = \\ &= 1 - g_{R1}^{(+)}(1-x)g_{R2}^{(-)}(x) + g_{R1}^{(+)}(1)g_{R2}^{(-)}(0) \end{aligned} \quad (34)$$

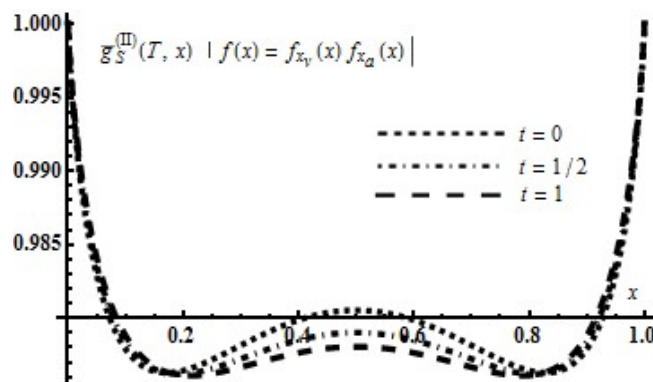
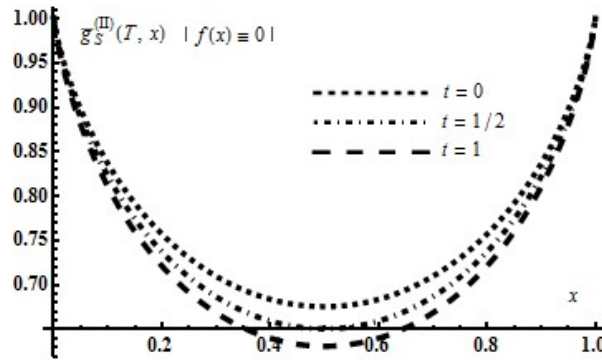


Figure 3: The Two Particles not Normalized Distribution Function  $g_S^{(II)}(T, x)$  with Considering of Interaction



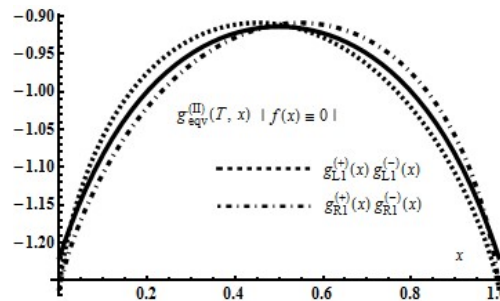
**Figure 4: The Two Particles not Normalized Distribution Function  $g_s^{(II)}(T, x)$  without Considering of Interaction**

Such distribution function under different values of temperature (this is dimensionless parameter  $t$ ) is depicted on the Figure 3 into form of two minimum symmetric curves.

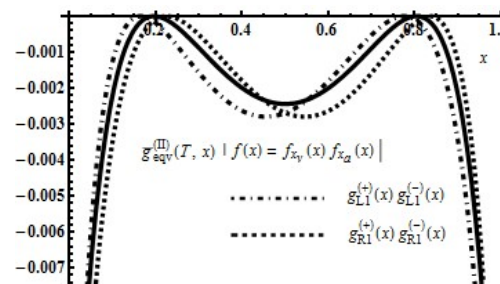
Without consideration of interaction between mixture component, when  $f(x) = 0$ , we're going to the two particle two sort the one minimum symmetrical distribution (Figure 4), which practically coincides with two particle one sort distribution (see subsection 2.1, Figure 2) despite the fact that analytical expressions (17) and (32) for density distribution something different among themselves in the reviewed case.

**The Informational and Thermodynamic Entropy. The Principle of Maximum of Lagrange Functional. The Equilibrium Distribution and Statistical Sum of Non-Interacting One Sort and Interacting Two Sorts Particles**

Without of usage the usual symmetrization procedure according to the (32) and (33) we have the two  $g_{L1}^{(+)}(x)g_{L2}^{(-)}(x)$  and  $g_{R1}^{(+)}(x)g_{R2}^{(-)}(x)$  non-symmetrical, relating to the constant (equilibrium) half value ( $x = 1/2$ ) of molar fraction of components, distributions (see Figure 5 is the without of considering of interaction ( $f(x) = 0$ )) and



**Figure 5: The Asymmetric of Two Particle Distribution Function Without Interaction (when  $t = 1/2$ ) and Equilibrium Product  $g_{eqv}^{(II)}(T, x)$  of given Different Sort One Particle Functions**



**Figure 6: The Asymmetric Two Particle Distribution Function with Interaction (when  $t = 1/2$ ) and Equilibrium Product  $g_{eqv}^{(II)}(T, x)$  of Given Different Sort One Particle Functions**

Figure 6 is the with considering of interaction ( $f(x) = f_{x_v}(x)f_{x_a}(x)$ ).

It is nature question is arriving: is it possible to receive the distribution function pass through the speculative operation of symmetrization? The answer according to overworking literature is positive [2-5,7].

For which purpose, let's define the informational entropy of two component mixture into approach of two particle interaction [7].

$$\sigma_L(x, T) = -Ln[\bar{g}_L(x, T)] \quad \sigma_R(x, T) = -Ln[\bar{g}_R(x, T)] \quad (35)$$

here

$$\bar{g}_L(x, T) = \frac{1}{N[\bar{g}_L]} \left[ 1 - g_{L1}^{(+)}(x)g_{L2}^{(-)}(x) - g_{L1}^{(+)}(0)g_{L2}^{(-)}(1) \right] \quad (36)$$

$$\bar{g}_R(x, T) = \frac{1}{N[\bar{g}_R]} \left[ 1 - g_{R1}^{(+)}(x)g_{R2}^{(-)}(x) - g_{R1}^{(+)}(1)g_{R2}^{(-)}(0) \right]$$

where  $N[\bar{g}_\gamma]$  is the norm of the defined distribution functions, which are opposite to the (33) not symmetrical of the normal but rationed (see subsection 2.1, expression (34)) two particle distribution, each of which satisfy the condition of fullness

$$\iint_{\delta} \bar{g}_\gamma(x, T) dx dt = 1, \quad \forall \gamma = \{L, R\}. \quad (37)$$

here  $T = T_{cr1} + t(T_{cr2} - T_{cr1})$  is the thermodynamic temperature,  $T_{cr1}$  and  $T_{cr2}$  are the corresponding critical values,  $t$  is the dimensionless temperature parameter,  $\delta = [0, 1]$  is the interval of integration.

The average entropy of mixture by the Shannon we can rewrite as<sup>5</sup>

$$\langle \sigma(T, x) \rangle = \frac{1}{2} \sum_{\gamma} \bar{g}_\gamma(x, T) \sigma_\gamma(x, T) = -\frac{1}{2} \sum_{\gamma} \bar{g}_\gamma(x, T) Ln[\bar{g}_\gamma(x, T)] \quad (38)$$

where  $\bar{g}_\gamma(x, T)$ ,  $\gamma = \{L, R\}$  is the corresponding probabilities of the  $\gamma$ -state of a two component mixture [2,7].

In such case the Boltzmann-Lagrange-Shannon functional under fullness condition (37) takes the form [3,6].

$$Z\{\bar{g}_L, \bar{g}_R\} = -\sum_{\gamma} \iint_{\delta} \bar{g}_\gamma(x, T) Ln[\bar{g}_\gamma(x, T)] dx dt - \beta(x, T) \sum_{\gamma} \left( \iint_{\delta} \bar{g}_\gamma(x, T) dx dt - 1 \right) \quad (39)$$

here  $\beta(x, T)$  is the unknown function (named as Lagrange product), which is necessary to find from the extreme

$$\delta Z\{\bar{g}_L, \bar{g}_R; \beta\} = 0 \quad (40)$$

of the first variation of functional (39), namely

$$\delta Z\{\bar{g}_L, \bar{g}_R\} = -\sum_{\gamma} \iint_{\delta} (1 + Ln[\bar{g}_\gamma(x, T)]) \delta \bar{g}_\gamma dx dt - \beta(x, T) \sum_{\gamma} \iint_{\delta} \delta \bar{g}_\gamma dx dt = 0. \quad (41)$$

The such condition is equivalent to the system of variations equations

$$\begin{cases} \delta Z\{\bar{g}_L, \bar{g}_R\} / \delta \bar{g}_L = -(1 + Ln[\bar{g}_L(x, T)]) - \beta(x, T) = 0 \\ \delta Z\{\bar{g}_L, \bar{g}_R\} / \delta \bar{g}_R = -(1 + Ln[\bar{g}_R(x, T)]) - \beta(x, T) = 0 \end{cases} \quad (42)$$

Which takes the sense only in the case, when

$$\bar{g}_{eqv}(x, T) \equiv \bar{g}_L^*(x, T) = \bar{g}_R^*(x, T) = \frac{1}{Exp[1 + \beta(x, T)]} \equiv \frac{1}{\Omega(T, x)} \quad (43)$$

where  $\Omega(T, x) = Exp[1 + \beta(x, T)]$  is the statistical sum of two component mixture,  $g_{eqv}(x, T)$  is the equivalent or equilibrium two particle distribution [2].

For founding of equilibrium distribution we can use the properties of the exponent expiation of the one particle distribution function ( $L(x) \equiv x Ln[x]$  and  $R(x) \equiv (1-x) Ln[1-x]$ ) (12) into Taylor's series, in particular

$$L(x) = \frac{1}{2} \ln \frac{1}{2} - F_1(x) + F_2(x) \quad R(x) = \frac{1}{2} \ln \frac{1}{2} + F_1(x) + F_2(x)$$

where  $F_1(x) = \sum_{k=1}^{\infty} F_{2k-1}(1/2)(x-1/2)^{2k-1}$  and  $F_2(x) = \sum_{l=1}^{\infty} F_{2l}(1/2)(x-1/2)^{2l}$  are not paired and paired part of the

functions  $L(x)$  and  $R(x)$  of the argument  $x$  correspondingly, for which the conditions of symmetry are satisfied

$$F_1(1-x) = -F_1(x) \quad F_2(1-x) = F_2(x)$$

and  $F_{2n-1}(1/2) = d_x^{2n-1} R(1/2) = -d_x^{2n-1} L(1/2)$   $F_{2n}(1/2) = d_x^{2n} R(1/2) = d_x^{2n} L(1/2)$  is the positive numbers ( $n=1, 2, \dots, \infty$ ).

If put the  $F_1(x) \equiv 0$ , then for the one particle the equivalent distribution functions we are gets the expressions

$$f_{x_v}^*(x, T) = Exp[\alpha(T) \frac{\langle M \rangle}{M_v} S(x)] \quad f_{x_a}^*(x, T) = Exp[\beta(T) \frac{\langle M \rangle}{M_v} S(x)] \quad (44)$$

where  $S(x) = \frac{1}{2} \ln \frac{1}{2} + F_2(x)$  is the symmetric parts  $L(x)$  and  $R(x)$ .

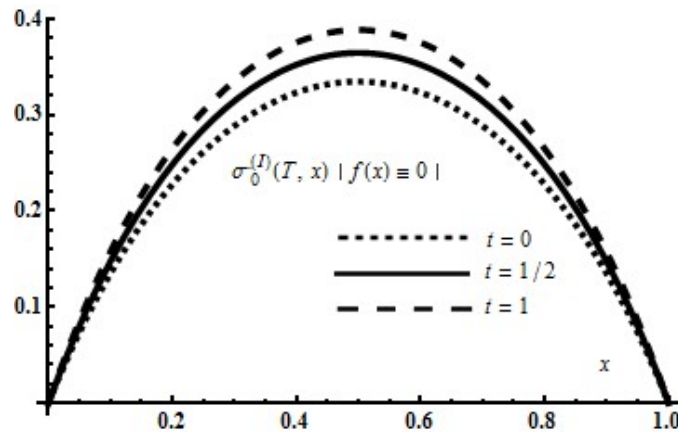
After substitution of received symmetrized one particle functions according to relations (19) and (34) we have equilibrium normal (not normalized) distributions  $g_{\text{eqv}}^{(I)}$  and  $g_{\text{eqv}}^{(II)}$  for two particles and one sort not interacting

$$\begin{aligned} \bar{g}_{\text{eqv}}^{(I)}(T, x) &\equiv 1 - \bar{g}_{x_v}^*(x) \bar{g}_{x_v}^*(x) - \bar{g}_{x_v}^*(0) \bar{g}_{x_v}^*(1) = \\ &= 1 - \bar{g}_{x_a}^*(x) \bar{g}_{x_a}^*(x) - \bar{g}_{x_a}^*(1) \bar{g}_{x_a}^*(0) \end{aligned} \quad (45)$$

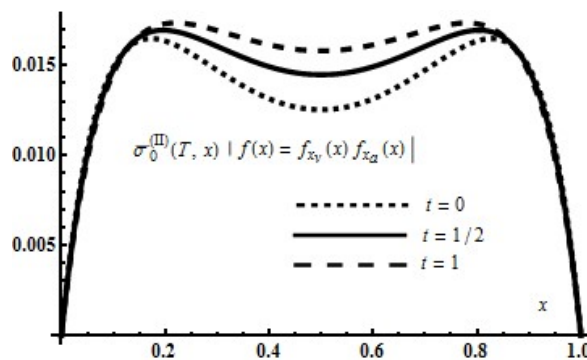
and two sorts of interacting

$$\begin{aligned} \bar{g}_{\text{eqv}}^{(II)}(T, x) &= 1 - \bar{g}_{L1}^*(x) \bar{g}_{L2}^*(x) + \bar{g}_{L1}^*(0) \bar{g}_{L2}^*(1) = \\ &= 1 - \bar{g}_{R1}^*(x) \bar{g}_{R2}^*(x) + \bar{g}_{R1}^*(1) \bar{g}_{R2}^*(0) \end{aligned} \quad (46)$$

components of mixture (see. For example Figure 5 and Figure 6 correspondingly, this is a continuous line)<sup>6</sup>, where  $\bar{g}_{x_\sigma}^*(x, T)$ , here  $\sigma = \{v, a\}$  and  $\bar{g}_{\gamma k}^*(x)$ , here  $\gamma = \{L, R\}$  and  $k = \{1, 2\}$  are respectively the one particle equilibrium distribution expressed by the relation (17) and (32).



**Figure 7: The Equilibrium Informational, A Two Particle of the One Sort Entropy  $\bar{\sigma}_0^{(I)}(T, x)$  for not Interacting Components of Water Vapour and Dry Air Mixture. пароповітряної суміші**



**Figure 8: The Equilibrium Informational, A Two Particle of the Two Sort Entropy  $\bar{\sigma}_0^{(II)}(T, x)$  for Interacting Components of Water Vapour and Dry Air Mixture. пароповітряної суміші**

The equilibrium of a one particle (35) informational entropy for two component water vapour and dry air mixture according to (43) and known functions of distributions (45) and (46) we can write into form

$$\bar{\sigma}_0^{(k)}(T, x) = -Ln[\bar{g}_{\text{eqv}}^{(k)}(x, T)] = Ln[\Omega_{(\kappa)}(T, x)], \quad (47)$$

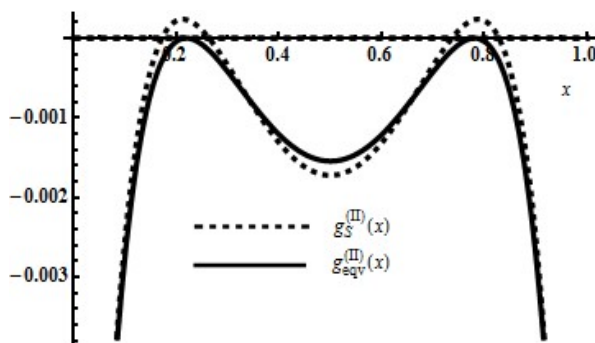
here  $\bar{\sigma}_0^{(k)}(T, x) \equiv \bar{\sigma}_L^{(k)}(T, x) = \bar{\sigma}_R^{(k)}(T, x)$ , where  $\kappa = \{I, II\}$  is the mute index of symbols for definition of interaction into mentioned

relation (47) for equilibrium informational entropy,  $\Omega_{(\kappa)}(T, x)$  is the statistical sum not interacting ( I ) and interacting ( II ) two component mixture.

From relation (43) according to known equilibrium distribution functions (45) and (46) it is following the expression for the statistical sum  $\Omega_{(\kappa)}$  of system and searching Lagrange's product  $\beta$  in accordance to conditions of extreme ( $\delta Z\{\bar{g}_L, \bar{g}_R; \beta\} = 0$ ) of the functional (39), hence

$$\Omega_{(\kappa)}(T, x) = 1 / \bar{g}_{\text{eqv}}^{(\kappa)}(T, x) \quad (\beta_k(x, T) = Ln[\Omega_{(\kappa)}(T, x)] - 1)$$

On the Figure 7 and Figure 8 is depicted the one particle equilibrium informational entropy (47) of two component water vapour and dry air mixture under conditions of absence ( $f(x)=0$  the case of I) and presence ( $f(x)=f_{x_v}(x)f_{x_a}(x)$  the case of II) interaction, correspondingly.



**Figure 9: The Abnormal Behaviour of the Two Particle of Different Sort Distribution Functions  $g_s^{(II)}(T, x)$  (33) at Critical Temperature of Boiling ( $t = 1$ ) in Comparison with Calculated for Relation (44) Equilibrium  $g_{equiv}^{(II)}(T, x)$  Two Particles Distribution Function**

Then the equilibrium one particle dimensionless entropy of two component  $\tilde{s}_{mix}^0$  (see Section 2, expr. (11)) under constant equilibrium values of pressure mixture  $\langle p \rangle$  (see Section 3) [7]. Temperature  $T$  which is determined in the right way must be match with defined according to (38) and calculated with usage of relations (45) and (46) the averaged informational entropy  $\langle \sigma \rangle$  of interacting mixture, from which we receive

$$\tilde{s}_{mix}^0(T, x) = \tilde{s}_{mix}^0 / \langle n \rangle \equiv \langle \sigma^{(k)}(T, x) \rangle \quad (48)$$

where

$$\begin{aligned} \langle \sigma^{(k)}(T, x) \rangle &= -\bar{g}_{equiv}^{(\kappa)}(x, T) \text{Ln}[\bar{g}_{equiv}^{(\kappa)}(x, T)] = \\ &= \Omega_{(\kappa)}(T, x)^{-1} \text{Ln}[\Omega_{(\kappa)}(T, x)] \end{aligned} \quad (49)$$

here  $\tilde{s}_{mix}^0(T, x)$  is dimensionless specific entropy of interacting two component mixture (11),  $\Omega_{(\kappa)}(T, x)$  is the statistical sum of the system (47),  $\langle n \rangle = \langle M \rangle / N_A$  is the average number of particles on the unit of mixture mass,  $\langle M \rangle = M_v M_a / (M_v + M_a)$  is the averaged molar mass of mixture and  $N_A$  is the Avogadro's number,  $k$  is the silent index, which points only on the absence (I) or presence (II) of interaction in the one dimensional probability model (the last one can be neglected without any reservations).

So we receive the dependence of specific entropy (on the one particle of unit mass) from molar fraction of component, which at module values in the case of I ( $f(x)=0$  than no interaction is present) something differences (the coefficient of similarities is  $\kappa \cong 0.44$ ) and in the case of II (the interaction is present) practically coincide with calculated for the expression (47) (see Figure 7 and Figure 8 correspondingly) in the mentioned temperature intervals of investigation, but is the mirrored relative to the abscissa axis.

## Conclusions

The normal view the symmetrized function of two particle distribution (18) and (33) (Figure 9, dashed line) is reflecting the temperature changes into two component interacted water vapour and dry air system at the neighbourhood of height critical temperature (boiling) not quite correct (the changes of the sign of distribution function at the maximal quantities), unlike the received into analogous way two particle distribution function (see relations (43) and (44)) according the equivalent or equilibrium distribution (Figure 9 solid line).

Determined analytically expressions (45) and (46) for calculation of equilibrium two particle distribution is adequate reacts on the temperature changes in the mentioned intervals of investigation (see. Figure 7,8, the increasing of entropy with increasing of temperature), but over the size of the big enough (symmetrical) neighbourhood equilibrium value ( $x = 1/2$ ) (see Figure 5,6, continuous line) may be incorrect to describe the properties of two component system near boundary values (at  $x = 0$  and  $x = 1$ ) of molar fraction of component, because the mentioned method of searching of equivalent distribution (44) is not fully well-founded and unambiguous.

The two component interacting system, which is partially investigated in this article, tends to transition from a two-minimum distribution form to a single minimum one as the thermodynamic temperature approaches the upper critical value (boiling). Unfortunately, we do not observe an ideal degeneration of the distribution function form (Figure 3) into a single-minimum one, since the interparticle interaction is not described at the molecular level.

The probabilistic estimates of the interaction between the components of the water vapour and dry air mixture performed in this publication in combination with the Boltzmann-Lagrange-Shannon extreme functional method provide a proper justification for the principle of maximum entropy and metastable states of thermodynamic equilibrium (see Figure 8, the interval between the two maxima) both in general and from the point of view of the external temperature effect on the two component system [6].

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## Foot Notes

1. Here lower index  $\sigma$  at  $x^*$  is deliberately rejected, because in the future we have applied the symmetrization procedure relatively to the type (v or a) of observed quantity.
2. In the future we are neglect by the symbol «\*» at definition of the fixed value for quantity  $x$  providing in general of meaning the last one quantity content as continuous value, because  $x_a = 1 - x_v$ .
3. Let's remark, that into the future subsections 2.1 and 2.2 with purpose of improvement of publication material for the temperature one particle distribution functions (12) it is taken the following equivalent definitions  $f_{x_v}^t(\xi) \equiv f_{x_v}(\xi, T)$  та  $f_{x_a}^t(\eta) \equiv f_{x_a}(\eta, T)$ , where  $t$  is the dimensionless temperature parameter. In the received expressions for probabilities and functions of density distribution the dependence from temperature sometimes is omitted so as not to clutter the formulas with unnecessary notation.
4. Let's denote, that symmetrization procedure for one particle distribution function (18) into the non-interacting two-component mixture it is necessary to applied, than normalization of such functions is performed only into range of the interval  $\delta = [0,1]$  through molar fraction of the component at the fixed temperature of mixture.
5. It should be noted, that such expression for entropy by the Shannon in the case when  $\bar{g}_\gamma(x, T) \equiv \bar{g}_{eqv}^\gamma(x, T)$ , where  $\bar{g}_{eqv}^\gamma(x, T)$  is the equilibrium distribution (see future relations (45) and (46)), under product on the Boltzmann  $k$  constant coincides, as it was demonstrated into works with the specific thermodynamic entropy  $s_{mix} = k \tilde{s}_{mix}^0 / \langle n \rangle = k \bar{s}_{mix}^0$  (9-11), so  $\bar{s}_{mix}^0(T, x) = \langle \sigma(T, x) \rangle$  [2,3].
6. Let's denote, that according to symmetry of one particle equivalent functions of distributions (44) into relations (45) and (46) we have  $\bar{g}_{x_v}^*(0)\bar{g}_{x_v}^*(1) \equiv \bar{g}_{x_a}^*(1)\bar{g}_{x_a}^*(0)$  and  $\bar{g}_{L1}^*(0)\bar{g}_{L2}^*(1) \equiv \bar{g}_{R1}^*(1)\bar{g}_{R2}^*(0)$ .