Comment on the ”Density profiles in the theory of condensation” (Physica A, 226 (1996) 117-136). Stationary profiles of the condensation

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The theory of the density profiles of condensation [1] leads to the radically new approach to the kinetics of the condensation process. The formalism presented in [1] is complete but one can make some simplifications in order to see how this theory transfers into the old theory with the integral style of the account of the vapor consumption. We shall call this old manner of account as the additive theory (AT).

The AT works in some conditions where the direct suppositions of this theory (the homogeneous character of the vapor consumption from the whole volume, the homogeneous profiles of the vapor density around the droplet) aren’t valid. The reason is rather simple and is based on the following important note For the validity of the AT it is necessary that the main substance is accumulated by the part of the profile where the decrease of the supersaturation is less or equal than $1/\Gamma$. The concrete form of spectrum isn’t important. It is necessary to know the integral over the whole distances and it is given due to the conservation of the substance by the number of the molecules inside the droplet.

The main numerical effect of the theory with the profiles of the condensation (PT) is attained due to the gap of the density near the droplet. One can see at least two opportunities to come to the additional regime:

- There is no gap near the droplet.
The gap exists, but the main part of the substance is accumulated by the tail of the profile where it is possibly to use formally the AT due to the previous note.

The first opportunity has conceptional significance and requires the special consideration. It was completely done in [1]. Here the possibility to grasp this situation is ensured by the universal character of the spectrum.

The second opportunity is automatically accounted by the PT. The additive character here can be seen if we take into account namely the integral definition of $\beta_{\text{eff}}$. The integral character of the definition of $\beta_{\text{eff}}$ instead of the level character of the definition of $\beta_{\text{st}}$, $\beta_{\text{fin}}$ allows to grasp the additive superposition of the long tails of the profile.

The additive character of the superpositions of the profiles is the main feature of the both limit situations described above. As it is stated in [2] (page 315) the first kinetic model is the most natural in the first situation. It is the corresponding model for the account of the additive character. So, it have to be the corresponding model for the second opportunity.

Despite the clear significance of the PT it is difficult for the experimenters to imagine the qualitative picture of the process and to compare the roles of the previous AT and the new PT. So, here some simplifications will be presented which will lead to more clear image of the process of condensation. One has to note that these simplifications are rather rough and ensure only the write qualitative character of the process. Certainly one can use directly the PT for the accurate results. The validity of the PT isn’t violated below.

Note that the leading idea of consideration of the condensation process is the avalanche character of kinetics. We shall use this property here once more.

According to the avalanche character the essential error in the quantity of the condensated substance leads to the rather small error in the number of the droplets. One can take here the total quantity of the substance or the the substance condensed in the separate droplet.

Also due to the avalanche character of the process one can speak about the characteristic size of the droplet, about the characteristic time scale of the period of the droplets formation, about the back front of the size spectrum.

We shall take for example the diffusion regime of the droplet growth. There is no need to consider the transition to the free molecular regime because it was completely discussed in [2].
All definitions can be found in [1].

1 The length of relaxation

...From the primitive formal point of view the stationary profile leads to the divergence of the substance consumed by the droplet (all the excess must be in the droplet) and for the superposition of the profiles from the other droplets. Really at the stationary profile \( n(\infty) - n(r) \sim r^{-1} \) which can not be integrated. So, the substance inside the droplet goes to \( \infty \). On the other hand the sum \( \sum \frac{1}{r} \) which presents the superposition of the profiles of the droplets lying on one line goes to \( \infty \) and this can not be appropriated.

It seems that it closes the problem of the stationary profiles. But the tails can be rather long and according to \( \int_1^\infty \frac{1}{x} dx \sim \ln(x) \to \infty \) can accumulate the main quantity of the substance.

We shall start from the AT. The evolution of the elementary perturbation can be described by the Green function of the free space

\[ G \sim \exp \left( -\frac{r^2}{4Dt} \right) \]

In a very rough approximation (we are going to present the trivial explanation) one can see the plane region \( r < \sqrt{4Dt} \) and the negligible tail \( r > \sqrt{4Dt} \).

On the base of this consideration one can say that

\[ R_{rel} = \sqrt{4Dt} \]

presents the characteristic length of relaxation. One can take for \( t \) the characteristic length of the period of the droplets formation \( t_1 \). Then one can say that \( r_{rel} \) can be treated as the length of the stationary profile of the vapor density.

In the AT for the finish of the droplets formation one can write

\[ N_{tot} \nu_1 = \Phi n_\infty / \Gamma, \quad (1) \]

where \( \nu_1 \) is the characteristic size of the droplets at the period of the droplets formation. Here \( \Phi \) marks some characteristic value of the supersaturation during the period of the droplets formation.
The mean distance between droplets can be estimated as

\[ R_{\text{mean}} = N_{\text{tot}}^{-1/3} \]

For the rate of the droplet growth one can take the ordinary law \[ 1 \]

\[ \frac{d\nu}{dt} \sim v_l^{1/2} (\Phi n_\infty D)^{3/2} t^{1/2} \]

and after the integration

\[ \nu \sim v_l^{1/2} \Phi^{3/2} D^{3/2} n_\infty^{3/2} t^{3/2} \]

Then

\[ v_1 \sim v_l^{1/2} \Phi^{3/2} D^{3/2} n_\infty^{3/2} t_1^{3/2} \]

Then after the substitution one can come to

\[ Dt_1 = \Gamma^{-2/3} \Phi^{-1/3} \left( \frac{v_l}{v_v} \right)^{-1/3} N_{\text{tot}}^{-2/3} \]

where \( v_v = n_\infty^{-1} \) is the volume for the molecule in the saturated vapor. This leads to

\[ R_{\text{rel}} = \Gamma^{-1/3} \Phi^{-1/6} \left( \frac{v_l}{v_v} \right)^{-1/6} R_{\text{mean}} \]

Introduce parameter

\[ \sigma = \Gamma^2 \left( \frac{v_l}{v_v} \right) \Phi \]

One can see that parameter \( \sigma \) can take the arbitrary values in comparison with 1. The inequality \( \Gamma \gg 1 \) can be compensated by the ordinary observed inequality \( v_l \ll v_v \).

In the bubbles formation one has to substitute \( v_v \) by \( v_l \) and \( v_l \) by \( v_v \) (\( \Phi \) here isn’t important). Then one have to come to \( \sigma \gg 1 \).

The final result will be

\[ R_{\text{rel}} = \sigma^{-1/6} R_{\text{mean}} \]

When \( \sigma \ll 1 \) one can use the stationary profile of density from the point of view of AT which ignores the non-stationarity of the tails of the profiles. The estimate will be given in the next section.

It is rather natural to say that it is sufficient to have the stationary profile at the distances \( R_{\text{mean}} \) (Certainly one can imagine that the tails in the superposition from the other droplets lying far (not neighbors) are very important and they are non stationary. The exclusion of this situation can be given analytically and it will be directly seen later.
2 The form of the stationary profile

Now we see that it is really interesting to investigate the stationary profiles of the density. The form of the profile is given by the very simple formula

\[ n_{st}(r) = n(\infty) - \frac{R_d}{r}[n(\infty) - n_{\infty}] \]

where \( R_d \) is the size of the droplet. It can be found by the

\[ R_d = \left( \frac{3\eta \nu}{4\pi} \right)^{1/3} \]

One can define now the boundary between the additive region and the non-additive region as the distance where

\[ \zeta(r) - \zeta(\infty) = \frac{\zeta(\infty)}{\Gamma} \]

One can see that this boundary (let us denote it via \( R_{add} \)) is equal to

\[ R_{add} = \Gamma R_d \]

Define by \( Q_{na} \) the quantity of the substance disappeared from the non-additive region

\[ Q_{na} = \int_{R_d}^{R_{add}} [n(\infty) - n(r)]d^3r \]

One can easily calculate this integral in the approximation of the stationary profile

\[ Q_{na} = \int_{R_d}^{\Gamma R_d} \frac{R_d}{r}[n(\infty) - n_{\infty}]4\pi r^2 dr = \frac{3}{2} \sigma \nu \]

From the last expression it is seen that for \( \sigma > 1 \) \( Q_{na} > \nu \) and the stationary approximation can not be valid for all \( r < R_{add} \).

Now it is clear that for \( \sigma > 1 \) one can not use the AT and has to use the PT. For \( \sigma < 1 \) the question is open now.

Consider these questions from the point of view of the PT. Having taken into account the mentioned representation for the Green function (certainly it is worth correcting it by the normalizing factor and the intensity of the vapor consumption) one can see by the analysis of the integrals of the type
\[ \int r^2 \exp(-r^2/4Dt)dr \] that the essential part of the substance is accumulated in the region with the stationary profile.\[ ]

When we speak about the essential part of the quantity we mean that this part is rather great and the ratio of this quantity to the total quantity doesn't attain 0 and 1 or go to these values. Due to the avalanche character of the process of condensation the substitution of the total quantity to the essential part doesn't lead to the great variation of the kinetics of the process.

With the help of the last remark now one can give the qualitative description of the profile. Until \( r < R_{rel} \) the profile is close to the stationary one. When \( r > R_{rel} \) the profile isn't so essential.

Consider the situation \( \sigma > 1 \). It seems that for the validity of the stationary approach one needn't to require that \( R_{rel} \geq R_{mean} \) but only that \( R_{rel} \geq \Gamma R_d \). Really, all tails at \( r > \Gamma R_d \) can be treated as corresponding to the additive region. Note, that there is absolutely no need to know the concrete form of the profile in the additive region but only the quantity condensed in this region (which is the total quantity (the number of the molecules in the droplet) except the quantity in the non-additive region (which can be at \( R_{rel} > \Gamma R_d \) easily calculated in the stationary approximation)).

To show that there is no profit to consider \( \Gamma R_d \) instead \( R_{mean} \) compare these two values.

For the AT we can use the known equality \( \square \) and come to

\[ \frac{R_{mean}}{\Gamma R_d} = \left( \frac{3}{4\pi} \right)^{1/3} \sigma^{-1/3} \]

This shows that for \( \sigma > 1 \) (when we have the problems with relaxation) the new estimate can not also lead to the relaxation for \( r < \Gamma R_d \) and there is no profit to use it.

As we have noted that the essential part of the condensed substance is taken from the distances corresponding to the stationary profile of the substance density we can introduce the distance \( R_s \) by the condition that

\[ \int_{R_d}^{R_s} n(\infty) - n_{st}(r)d^3r = \nu \]

\(^1\)One has to calculate the Green function with the factor coming from the intensity of the vapor consumption. The integral will be with another power of the pre-exponential factor but the final conclusion about the essential part will remain valid.
Calculate this distance. Then

\[ R_s = \left( \frac{2}{3\sigma} \right)^{1/2} \Gamma R_d \]

or

\[ R_s = (2/3)^{1/2}(4\pi/3)^{1/3}\sigma^{-1/6} R_{mean} \]

or

\[ R_s = (2/3)^{1/2}(4\pi/3)^{1/3} R_{rel} \]

The absence of the parameters in the last equation is important and is necessary for the validity of the statement that the essential part of the condensed substance comes from the distances with the stationary profile.

3 Situation \( \sigma < 1 \)

In the opposite situation \( \sigma > 1 \) the AT has no perspectives because even in the non-additive region the stationary distribution is going to be violated\(^2\).

In the situation \( \sigma < 1 \) the naive interpretation of the boundary of the exhausted region in the PT will lead to the big error. Really at \( \sigma < 1 \) the main quantity of the consumed substance is in the additive region. One can see this from expression (2) which can be used due to the stationary character of the profile in the non-additive region in this situation.

So, one has to use the integral definition of the boundary of the exhausted region as it was done in [1] in the definition of \( \beta_{\text{eff}} \). The reason of the integral style of the definition of \( \beta_{\text{eff}} \) instead of the level definition of \( \beta_{\text{st}} \) and \( \beta_{\text{fin}} \) is to grasp the situation with the essential long tails of the density profile. But in the additive region there is no need to speak about the overlapping of the exhausted regions. So, one has to use the first model as it was done in [2], page 315. The closeness of the results of all models guarantees the universal form of the condensation kinetics.

Now we can show how to see the transition of the AT to the PT. One can explicitly calculate the effect from the gap in the stationary approximation (which can be used when \( \sigma < 1 \)) by the integration. The remarkable fact is

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\(^2\) The stationary distribution will be violated at the end of the non-additive region. This end will be attained due to the violation of the profile which goes to be the small one but not when the excess of stationary profile goes to cross the level \( n_{\infty} \zeta/\Gamma \).
that the quantity of the substance \( Q_{hna} \) accumulated from the region \( r < \Gamma R_d \) with the layer \( \Phi n_\infty / \Gamma \) (this comes from the formal interpretation of the AT as the theory with the exhausted regions) is comparable with \( Q_{na} \)

\[
Q_{hna} = \frac{2}{3} Q_{na}
\]

Then the asymptotical account of the gap can be attained by the renormalization of the quantity of the substance accumulated by one droplet

\[
Q \to Q(1 - \frac{1}{2}(\frac{\Gamma R_d}{R_{\text{mean}}})^{1/3})
\]

This leads to the renormalization at \( \sigma \ll 1 \) for the total number of the droplets

\[
N_{tot} \to N_{tot}(1 + \frac{2}{5} \frac{1}{2}(\frac{\Gamma R_d}{R_{\text{mean}}})^{1/3})
\]

**References**

[1] V.Kurasov Physica A 226 (1996) 117-136

[2] V Kurasov, Universality in kinetics of the first order phase transitions, Chemistry Research Institute of St.Petersburg University, St.Petersburg, 1997, 400 p.