

Stochastic Theory of Nucleation in Open Molecular Systems

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In generalization of earlier developments [13, 16] the formation of clusters in open systems which exchange work and/or molecules with the surroundings is investigated.

It is shown that in the case of cluster formation under isobaric-isenthalpic conditions the function $(S-pV/T)$ is the relevant thermodynamic potential of this process. Further are considered conditions of continuous supply of monomers and removal of large clusters. The master equation of cluster formation under these conditions is established, and the thermodynamic and molecular processes going on are qualitatively discussed.

In Verallgemeinerung vorangegangener Arbeiten [13, 16] wird die Bildung von Clustern in offenen Systemen untersucht, die mit der Umgebung Arbeit und/oder Moleküle austauschen.

Für den Fall der Clusterbildung unter isobar-isenthalpischen Bedingungen wird gezeigt, daß $(S-pV/T)$ das relevante thermodynamische Potential dieses Prozesses darstellt.

Ferner werden Bedingungen betrachtet, bei denen ständig Monomere zugeführt und große Cluster abgeführt werden. Die Mastergleichung der Clusterbildung unter diesen Bedingungen wird formuliert und eine qualitative Diskussion der ablaufenden thermodynamischen und molekularen Prozesse gegeben.

1. Introduction

Going back to the twenties of our century, the “Zeitschrift für physikalische Chemie” was one of the main scientific journals for nucleation phenomena: In 1926 Volmer and Weber [1] gave a first quantitative description of the nucleation rate, which was followed by Farkas [2] in 1927, who improved the kinetic description. In 1934 important papers of Volmer and Flood [3] and of Kaishev and Stranski [4] were published in Z. phys. Chemie, and in 1940 Neumann and Döring [5] published about nucleation in binary vapors. This enumeration is rather incomplete and shall mark only some steps in the development of nucleation theory, which are close connected with this journal.

But despite an intensive research over a period of about sixty years a number of problems of the whole process of nucleation, growth, Ostwald ripening and coagulation of clusters remain not finally solved yet.

For instance, the cluster formation in open systems is of considerable interest for many applications especially to modern surface technology [6]. This has attracted many experimentators and theoretical workers to this field [7–12].

In a foregoing paper [13] we have developed a relatively simple model for the thermodynamic and molecular processes in conically expanding nozzle beams entering into a vacuum. Here we consider two other conditions of openness.

First we investigate molecular systems under isobaric-isothermal and isobaric-isenthalpic conditions. We will show that the main features of the theory developed in our earlier works [11–13] remain valid if the entropy S is replaced by the thermodynamic potential $S - pV/T$. The new procedure takes into account the work which the gas has to carry out against the external pressure.

At second we consider a pumped open system with an influx of monomers and an outflux of very big clusters. Such a situation may be realized in a rough model of rain. We will show how the classical theory of Becker and Döring [14] can be derived from the modern stochastic theory.

2. Thermodynamics and equilibrium probability distribution

In the following we consider a closed system in the gaseous state, consisting of a condensable vapor. The total number of particles is denoted by N_{tot} .

Due to interactions between the particles a number of particles of the vapor is bound in clusters, resulting in a discrete distribution of clusters and free particles. This distribution is described by the vector \mathbf{N} :

$$\mathbf{N} = \{N_1 N_2 \dots N_n \dots N_N\} \quad (2.1)$$

N_1 is the number of free particles of the condensable vapour (monomers), N_2 the number of bound states of two particles (dimers) and so on.

If the total number of particles in the system is kept constant it holds:

$$N_{\text{tot}} = \sum_{n=1}^N n N_n = \text{const.} \quad (2.2)$$

where n is the number of condensable particles bound in the cluster, the number of clusters consisting of n particles is denoted by N_n .

From a statistic point of view every possible distribution \mathbf{N} is found with a certain probability for a given time, defined by

$$P(\mathbf{N}, t) = P(N_1 N_2 \dots N_n \dots N_N, t). \quad (2.3)$$

In a stochastic theory the formation and growth of clusters can be described by the change of $P(\mathbf{N}, t)$ in time. Let us study first the equilibrium probability distribution $P^0(\mathbf{N})$.

In thermodynamic equilibrium the probability $P^0(\mathbf{N})$ to find a certain distribution of clusters in the bath of the free particles is defined by the following relation:

$$P^0(\mathbf{N}) = \int_{C(\mathbf{N})} \varrho^0(q_1 \dots p_N) dq_1 \dots dp_N. \quad (2.4)$$

Here $\varrho^0(q_1 \dots p_N)$ means the equilibrium probability distribution for the N particles in the spatial and momentum coordinates of all particles. The integration is carried out for the subspace $C(\mathbf{N})$ of the assumed particle configuration \mathbf{N} . $\varrho^0(q_1 \dots p_N)$ depends on the thermodynamic boundary conditions of the system. Let us summarize the following cases:

(a) Isochoric conditions

This situation has been discussed in our previous papers with respect to the isothermal case ($T, V, N_{\text{tot}} = \text{const.}$) [11, 15] and to the isoenergetic case ($U, V, N_{\text{tot}} = \text{const.}$) [12, 13, 16]. As the results we have found:

$$(i) P^0(\mathbf{N}) = \exp\{[F(T, V, N_{\text{tot}}) - F(T, V, N_1 N_2 \dots N_N)]/k_B T\} \quad (2.5)$$

for $T, V, N_{\text{tot}} = \text{const.}$

where F is the free energy of the system.

$$(ii) P^0(\mathbf{N}) = \exp\{[S(U, V, N_1 N_2 \dots N_N) - S(U, V, N_{\text{tot}})]/k_B\} \quad (2.6)$$

for $U, V, N_{\text{tot}} = \text{const.}$

where S is the entropy of the system.

(b) Isobaric conditions

This case seems to be of more relevance for experimental conditions. In comparison to the discussion above we must consider the exchange of work with the surroundings, and therefore for $\varrho^0(q_1 \dots p_N)$ yields:

$$(iii) \varrho^0(q_1 \dots p_N) = C \exp\{-[\kappa(q_1 \dots p_N) + pV]/k_B T\} \\ \text{for } T, p, N_{\text{tot}} = \text{const.} \quad (2.7)$$

$$(iv) \varrho^0(q_1 \dots p_N) = \begin{cases} \text{const.} & \text{for } H - \delta H \leq \kappa(q_1 \dots p_N) \leq H + \delta H \\ 0 & \text{else} \end{cases} \quad (2.8) \\ \text{for } H, p, N_{\text{tot}} = \text{const.}$$

$\kappa(q_1 \dots p_N)$ is the Hamiltonian of the N particles system, H is the enthalpy and δH the thickness of the enthalpy shell. The constant is connected to

the volume of the microshell Ω^* which is related to the entropy S^* of the N particles system considered as a function of H and p . From

$$S^*(H, p, N) = k_B \ln \int d\Omega^*, d\Omega^* = dq_1 \dots dq_N dp_1 \dots dp_N \quad (2.9)$$

follows

$$\text{const.} = 1/\Omega^* = \exp\{-S^*(H, p, N)/k_B\}. \quad (2.10)$$

In relations given above, p is the external pressure and V the volume of the system. Of course, the actual value of V depends on the cluster distribution \mathbf{N} , but not on the space and momentum coordinates. For an integration over the subspace $C(\mathbf{N})$ – that means a definite cluster distribution – $S^*(H, p, N)$, p and $V(\mathbf{N})$ are constants and contribute only to the prefactor of the integrals.

In order to get the equilibrium probability distribution [Eq. (2.4)] we integrate over all particle configurations compatible with the existence of the cluster distribution N . In this way we get with Eq. (2.7)

$$\text{(iii) } P^o(\mathbf{N}) = \exp\left\{\frac{G(p, T, N)}{k_B T}\right\} \cdot \int_{C(\mathbf{N})} \exp\{-[\varkappa(q_1 \dots p_N) + pV]/k_B T\} d\Omega^* \quad (2.11)$$

which gives

$$P^o(N_1 N_2 \dots N_N) = \exp\{[G(p, T, N_{\text{tot}}) - G(p, T, N_1 N_2 \dots N_N)]/k_B T\} \\ \text{for } T, p, N_{\text{tot}} = \text{const.} \quad (2.12)$$

with the thermodynamic potential

$$G(T, p, \mathbf{N}) = -k_B T \ln\{\exp(-pV/k_B T) \int_{C(\mathbf{N})} \exp[-\varkappa(q_1 \dots p_N)k_B T] d\Omega^*\} \\ = pV(\mathbf{N}) + F(T, V, \mathbf{N}) \quad (2.13)$$

where G is the free enthalpy of the system.

Starting from Eq. (2.8), we get in agreement with [16]

$$\text{(iv) } P^o(N_1 N_2 \dots N_N) = (1/\Omega^*) \int_{C(\mathbf{N})} d\Omega^* \quad (2.14)$$

which results in

$$P^o(N_1 N_2 \dots N_N) = \exp\{[S^*(H, p, N_1 N_2 \dots N_N) - S^*(H, p, N_{\text{tot}})]/k_B\} \quad (2.15)$$

where

$$S^*(H, p, N_1 N_2 \dots N_N) = (1/\Omega^*) \int_{C(\mathbf{N})} d\Omega^* \quad (2.16)$$

is the entropy of the cluster distribution for the given thermodynamic constraints. For systems with a linear dependence $S = S(U)$ it holds

$$S^*(H, p, \mathbf{N}) = S^*\{H(U, V), p(U, V), \mathbf{N}\} = S(U, V, \mathbf{N}) - pV(\mathbf{N})/T. \quad (2.17)$$

This relation is true especially for ideal systems.

As to be seen in Eqs. (2.5), (2.6), (2.12), (2.15) under thermodynamic conditions the equilibrium probability distribution is determined by thermodynamic potentials, which depend on the constraints. Thus we may write generally:

$$P^o(N_1 N_2 \dots N_N) \sim \exp[-\phi(N_1 N_2 \dots N_N)/k_B] \quad (2.18)$$

where $\phi(\mathbf{N})$ has to be specified in dependence on the thermodynamic constraints.

3. Master equation and detailed balance

Let us formulate now the master equation for the relaxation into the equilibrium state.

The kinetics of nucleation is assumed as an Markovian discrete process. The dynamics of the probability $P(\mathbf{N}, t)$ to find a certain cluster distribution \mathbf{N} at time t obeys a master equation:

$$\frac{\partial P(\mathbf{N}, t)}{\partial t} = \sum_{(\mathbf{N}')} \{w(\mathbf{N}|\mathbf{N}') P(\mathbf{N}', t) - w(\mathbf{N}'|\mathbf{N}) P(\mathbf{N}, t)\}. \quad (3.1)$$

The quantities $w(\mathbf{N}'|\mathbf{N})$ are the transition probabilities per unit time for the transition from \mathbf{N} to \mathbf{N}' . \mathbf{N}' specifies those distributions which are attainable from the assumed distribution \mathbf{N} .

The stationary solution of the master equation requires that $\partial P(\mathbf{N}, t)/\partial t = 0$. From this condition we find $\sum_{\mathbf{N}'} J(\mathbf{N}|\mathbf{N}') = 0$ with $J(\mathbf{N}|\mathbf{N}') = w(\mathbf{N}|\mathbf{N}') P(\mathbf{N}', t) - w(\mathbf{N}'|\mathbf{N}) P(\mathbf{N}, t)$ being the probability flux between the states \mathbf{N}' and \mathbf{N} .

Since the system is not pumped, the system is of potential type and the equilibrium condition is given by the more restricted condition of detailed balance. It means $J(\mathbf{N}|\mathbf{N}') = 0$ resulting in:

$$w(\mathbf{N}|\mathbf{N}') P^o(\mathbf{N}') = w(\mathbf{N}'|\mathbf{N}) P^o(\mathbf{N}). \quad (3.2)$$

Inserting Eq. (2.14), Eq. (3.2) results in:

$$w(\mathbf{N}|\mathbf{N}') = w(\mathbf{N}'|\mathbf{N}) \exp\{[\phi(\mathbf{N}') - \phi(\mathbf{N})]/k_B\}. \quad (3.3)$$

Due to the strong relation between the transition probabilities $w(\mathbf{N}|\mathbf{N}')$ and $w(\mathbf{N}'|\mathbf{N})$ via the thermodynamic potential only a kinetic assumption for one of the transition probabilities is necessary.

We assume that the growth and shrinkage of a cluster is due only to an attachment or evaporation of monomers of the condensable vapor.

In order to determine the transition probability for the attachment of a monomer to a cluster of size n , we assume in agreement with previous

papers [11 – 13, 15 – 17] that the probability increases with the surface area of the cluster, with the number of clusters of size n and with the density of the free particles of the vapour. In this way we get for the special process of attachment

$$\begin{aligned} w(\mathbf{N}'|\mathbf{N}) &= w(N_1 - 1 \dots N_n - 1 N_{n+1} + 1 \dots N_N | N_1 \dots N_n N_{n+1} \dots N_N) \\ &\equiv w_n^+ (N_1 N_n) = \alpha(T) n^{2/3} N_n N_1 / V. \end{aligned} \quad (3.4)$$

The parameter α determines the time scale of the stochastic processes. One has to consider further the specific properties of the surface, like surface tension σ , composition of the surface and the sticking coefficient.

We note, that the transition probabilities for the growth of clusters of different sizes are correlated, since the total number of particles in the system is kept constant [11, 12].

This means consequently for the master equation (3.1) that the probability $P(\mathbf{N}, t)$ does not factorize.

The transition probability for the opposite process, the evaporation of a monomer from the cluster surface, can be determined by means of Eq. (3.3).

4. Cluster formation in systems pumped with monomers

In pumped systems which have no thermodynamic potential, the condition of detailed balance (3.3) which connects the forward with the backward transition rates, does not hold further. Therefore, in general the theory of nucleation developed above will break down.

However, under special conditions at least some parts of the detailed balance condition still holds. That is the case, which we mentioned in the introduction as the rain model. It makes the same assumptions as in the derivation of the classical nucleation theory [18]:

- (i) The systems is pumped by an influx of monomers.
- (ii) Clusters, which are bigger than a certain size n^* , are removed from the system – that means an outflux of bound particles.
- (iii) If certain relations between influx and outflux hold (e.g. equal mass flows and balance between entropy production and export) the system may reach a stationary non-equilibrium state. In this state all numbers of clusters and free particles are kept constant.

For physical reasons we may exclude any changes in the transition probabilities of cluster growth and shrinkage except those, which are connected with the influx of monomers and the outflux of the biggest clusters.

Let us now discuss the consequences for the kinetic description by means of the master equation.

It has been pointed out [15] that the kinetic Eq. (3.1) for $P(N_1, N_2, \dots, N_N, t)$ can be reduced to a kinetic equation for the stochastic evolution of a single cluster. Therefore, we introduce the probability $P(n|N_1 + n, t)$ to find a cluster of size n in the bath of N_1 monomers at time t .

If we restrict ourselves to the evolution of a single cluster, while fix the distribution of the other clusters, the value $N_1 + n$ is a constant for the growth and shrinkage of the single cluster:

$$N_1 + n = (N_1 - 1) + (n + 1) = (N_1 + 1) + (n - 1). \quad (4.1)$$

For a reduction of the master Eq. (3.1) we now propose the following ansatz:

$$\frac{\partial P(N_1, N_2, \dots, N_N, t)}{\partial t} = \frac{\Gamma_N(t)}{N_2! \dots N_N!} \prod_{n=2}^N [P(n|N_1 + n, t)]^{N_n} \quad (4.2)$$

with

$$N_1 = N_{\text{tot}} - \sum_{n=2}^N n N_n \quad (4.3)$$

in the case of a closed system with a constant total particle number. It yields now:

$$\begin{aligned} \frac{\partial P(n|N_1 + n, t)}{\partial t} = & \{w^+(n-1) P[n-1|(N_1+1) + (n-1), t] \\ & + w^-(n+1) P[n+1|(N_1-1) + (n+1), t] \\ & - [w^+(n) + w^-(n)] P(n|N_1 + n, t)\} \end{aligned} \quad (4.4)$$

and

$$\frac{\partial \Gamma_N(t)}{\partial t} = -\Gamma_N(t) [w^+(1) P(1|N_1 + 1, t) - w^-(2) P(2|N_1 + 2, t)]. \quad (4.5)$$

The transition probabilities are defined as follows:

$$\begin{aligned} w^+(1) &= w_1^+(N_1) \\ w^+(n) &= w_n^+(N_1, N_n)/N_n \\ w^-(n) &= w_n^-(N_n)/N_n. \end{aligned} \quad (4.6)$$

Eq. (4.4) is the master equation for the evolution of a single cluster; whereas Eq. (4.5) is the balance equation for the probability of the free monomers. It realizes the different boundary conditions.

In the case of an open stationary system with permanent influx of monomers we have

$$0 = -\Gamma_N(t)[w^+(1)P(1|N_1 - 1, t) - w^-(2)P(2|N_1 - 2, t) + J^s] \quad (4.7)$$

J^s means the probability flux which results from the influx of monomers and ensure the constant number of free particles. The r.h.s. of Eq. (4.7) just vanishes, therefore we have $\partial\Gamma_N/\partial t = 0$, that means Γ_N is a constant. Then Eq. (4.2) for $P(N_1, N_2, \dots, N_n, t)$ factorizes and the evolution of the cluster distribution can be completely described by the stochastic evolution of single clusters. That means only for the special condition of a constant influx of monomers we are able to reduce the complicated master Eq. (3.1) to a Beker-Döring like equation of independently growing clusters.

Eq. (4.4) can be now discussed in the same way as proposed by Becker and Döring in 1935 [14]. The stationary solution of Eq. (4.4) is given by $\partial P(n, t)/\partial t = 0$. [In the following we denote $P(n|N_1 + n, t) \equiv P(n, t)$], resulting in:

$$J(n+1|n) = w^+(n)P(n, t) - w^-(n+1)P(n+1, t) = J^s = \text{const.} \quad (4.8)$$

J is the probability flux between the states n and $(n+1)$; in the stationary case it is a constant.

Eq. (4.8) means a recursive system of equations in order to determine the stationary probability $P^s(n)$ [17]:

$$P^s(n) = P^s(a) \prod_{j=a+1}^n b(j) - J^s \sum_{k=a}^{n-1} Q(k) \quad (4.9)$$

with

$$b(j) = w^+(j-1)/w^-(j) \quad (4.10)$$

$$Q(k) = \frac{1}{w^+(k)} \prod_{i=k+1}^n b(i). \quad (4.11)$$

With respect to the conditions (i), (ii) of this chapter we assume

$$P^s(1) = \text{const.}; P^s(n^*) = 0 \quad (4.12)$$

that means n^* is an absorber state. The stationary flux is then given by the expression:

$$\frac{J^s}{P^s(1)} = \prod_{j=2}^{n^*} b(j) / \sum_{k=1}^{n^*-1} Q(k) \quad (4.13)$$

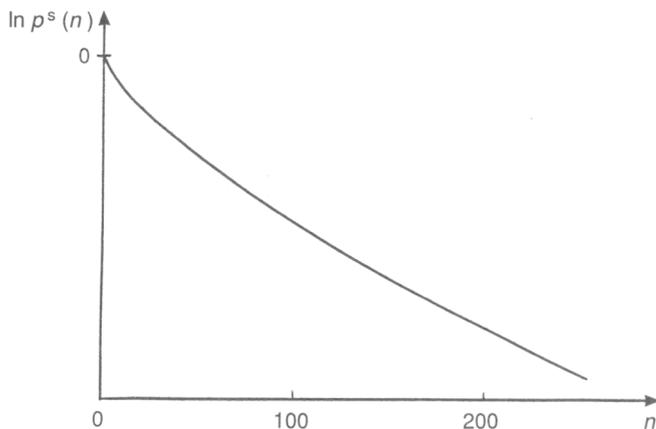


Fig. 1. Stationary probability distribution $p^s(n) = P^s(n)/P^s(1)$ versus cluster size n . $n^* = 250$.

which can be reduced by means of the assumptions of the classical nucleation theory to a formula like the classical nucleation rate.

Introduction the normalized probabilities $p^s(n) = P^s(n)/P^s(1)$, we arrive finally at the stationary probability in the form:

$$p^s(n) = p^s(a) \prod_{j=a+1}^n b(j) - \prod_{j=2}^{n^*} b(j) \sum_{k=a}^{n-1} Q(k) / \sum_{k=1}^{n^*-1} Q(k) \quad (4.14)$$

which is completely determined by the transition rates of the single cluster.

5. Discussion

In this work we have shown how the stochastic theory of cluster kinetics in open systems may be based on Gibbs equilibrium distributions.

At first we have derived that under isobaric-isothermal conditions and under isobaric-isenthalpic conditions the role of the energy U is taken over by the enthalpy $H = U + pV$ and that the role of the entropy is taken over by the thermodynamic potential $S^*(H, p, \mathbf{N}) = S(U, V, \mathbf{N}) - pV/T$.

At second we investigated the stationary state in a system which is pumped by an influx of monomers, and where on the other side big clusters are removed from the system. Such a situation is typical e.g. for rain phenomena.

In this case the stationary probability distribution of clusters (Fig. 1) is monotonously decreasing with the cluster size and ends at the maximum size n^* .

As also shown in Fig. 1 the distribution shows a long tail with a scaling like

$$\ln P^s(n) \sim C_1 - C_2 n^{(1+\varepsilon)}, \varepsilon > 0.$$

For large n^* this behaviour reminds of the properties observed in the phenomena of self-organized criticality [19] which are characterized by structures on all scales. Whether such a relation between S.O.C. and the cluster kinetics in "rain systems" exists, needs further investigations.

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