Rostocker Physikalische Manuskripte, Heft 9 (1986)

On the Droplet Formation in Dependence on Thermodynamic Constraints

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1. Introduction

We consider a closed and finite system with N free particles being an ideal gas mixture. We fix the thermodynamic constraints

$$N = \text{const}, \; V = \text{const}, \; T = \text{const} \qquad (1)$$

in such a way that the pressure of the supposed ideal vapor

$$p = \frac{N}{V} k_B T \qquad (2)$$

is larger than the equilibrium pressure $p_\infty(T)$ of the saturated vapor, that means the system is in a supersaturated state. We define the initial supersaturation y as follows:

$$y = \frac{p}{p_\infty} = \frac{N k_B T}{p_\infty V} \qquad (3)$$

To reach the equilibrium state the system shall be able on principle to undergo a phase transition. If the initial state is a metastable one, that means there exists an energy barrier for the phase transition, the phase separation takes place by a nucleation process, where an overcritical droplet is formed. Undercritical droplets diminish again.

This paper deals with the problem how to choose the thermodynamic parameters respectively the initial supersaturation

(i) to find an overcritical droplet at all

(ii) to obtain a droplet being more stable than the initial vapor phase

(iii) to change the nucleation process into a spinodal decomposition, that means the nucleation barrier is diminishing.

2. Kinetic Description of the Droplet Evolution

We suppose that a single droplet has formed in the system and evolves due to the following kinetic mechanism:

$$\begin{aligned} A_1 + A_l &\underset{w^-}{\overset{w^+}{\rightleftarrows}} A_{l+1} \\ (N-l)A_1 &\underset{w^-}{\overset{w^+}{\rightleftarrows}} (N-l-1)A_1 \end{aligned} \qquad (4)$$

l is the number of particles bound in the droplet ($l \leqq N$). Both reactions (4) are coupled by the limitation of the overall particle number.

The droplet evolution is assumed to be a Markovian birth and death process. If we define P(l,t) to be the probability to find the droplet with l particles at the time t, then the following master equation describes the time evolution of P(l,t):

$$\begin{aligned} P(l,t) = {} & w^+(l-1)\, P(l-1,t) + w^-(l+1)\, P(l+1,t) - \\ & - P(l,t) \left[w^+(l) + w^-(l) \right] \end{aligned} \qquad (5)$$

w^+ and w^- are the transition probabilities per unit time as also introduced in (4). We define them as follows:

$$\begin{aligned} w^+(l) &= \alpha\, l^{2/3} \, \frac{N-l}{V} \\ w^-(l) &= \alpha\, l^{2/3} \, \Lambda_1^{-3} \exp\left[\frac{f_l - f_{l-1}}{k_B T} \right] \end{aligned} \qquad (6)$$

Λ_1 is the de Broglie wave length of the free particle and f_l is a potential function: $f_l = -Al + Bl^{2/3}$ with $f_1 = 0$ and

$$A = -k_B T \ln \frac{p_\infty}{k_B T} \Lambda_1^3 \; ; \; B = 4\pi (4\pi c_\alpha / 3)^{-2/3} \sigma \qquad (7)$$

α is a constant with respect to the special properties of the droplet like the liquid density c_α [particles/m^3]; the surface tension σ and the temperature T.

Computer simulations with the given transition probabilities demonstrate the several stages of the stochastic evolution of the droplet during the phase transition. But in this paper we are only interested in the equilibrium probability distribution.

3. Equilibrium Distribution and Extremum Condition

The equilibrium distribution $P^o(l)$ we obtain from eq. (5) with the condition of detailed balance:

$$w^+(l)\ P(l,t) = w^-(l+1)\ P(l+1,t) \tag{8}$$

It yields:

$$P^o(l) = P^o_N \prod_{j=2}^{\ell} \frac{w^+(j-1)}{w^-(j)} \tag{9}$$

with the normalization

$$P^o_N = \left[1 + \sum_{n=2}^{N} \prod_{j=2}^{N} \frac{w^+(j-1)}{w^-(j)} \right]^{-1}$$

If we introduce a stationary potential

$$\phi_s(l) = -\ k_BT \ln \sum_{j=2}^{\ell} \frac{w^+(j-1)}{w^-(j)} \tag{10}$$

eq. (9) results in:

$$p^o(l) = P^o_N \exp\left[- \frac{\phi_s(l)}{k_BT} \right] \tag{11}$$

Note, that in the considered case $\phi_s(l)$ corresponds to the change of the free energy by the formation of the droplet with size l in the system.

Due to the thermodynamic parameters $P^o(l)$ can be a bimodal or an unimodal distribution. The existence of two maxima represents the coexistence of the vapor phase (l=1) and the droplet phase ($l=l_{st}$) where the stable droplet size is defined by the right maximum of $P^o(l)$ (see fig. 1). The minimum of $P^o(l)$ is relative to the critical droplet size l_{cr} caused by the nucleation barrier, where $\phi_s(l)$ has got its maximum.

To obtain an equation which gives a relation between the extremum droplet states and the thermodynamic parameters respectively the supersaturation we use the extremum condition of $P^o(l)$ in the form

$$P^o(l^E) = P^o(l^E+1)$$

and get with the condition of detailed balance (8) the extremum condition:

$$\ln\left(\frac{l^E}{l^E+1}\right)^{2/3} + \ln \frac{N-l^E}{V} \lambda_1^3 = \frac{1}{k_BT}(f_{l^E+1}-f_{l^E}) \tag{12}$$

By introduction of the droplet radius r instead of the bound particle number l

$$r^3 = (4\pi c_\alpha/3)^{-1}\ l$$

it yields approximately from eq. (12)

$$\ln \frac{(N-4\pi c_\alpha/3\ r_E^3)k_BT}{p_\infty V} = d_o \frac{1}{r_E} \tag{13}$$

where $d_o = 2\sigma(c_\alpha k_BT)^{-1}$ is the capillary length (for liquids normally about 10 Å).

Eq. (13) possesses two or one or no solution for r_E in dependence on the thermodynamic parameters. It shall be discussed now to determine the conditions for the existence of a droplet in the system.

4. Discussion

(i) First we investigate the conditions where an overcritical droplet has to be expected on principle in the system. That is the case when the bimodality of $P^o(l)$ is observed. This bimodality is just diminishing if $l_{cr} = l_{st}$, that means eq. (13) has only one solution. Thus we find the critical supersaturation y_{cp} for the initial system

$$y_{cp} = \exp\left[\left(\frac{4\pi c_\alpha/3}{N/4}\right)^{1/4} \left(\frac{4}{3} d_o\right)^{3/4} \right] \tag{14}$$

For $y < y_{cp}$ the system possesses only one (meta)stable state due to the vapor phase, where no overcritical droplet is able to be formed, while for $y > y_{cp}$ a stable droplet is possible to exist. That means y_{cp} has to reached at least initially to insert the nucleation process. That's why y_{cp} gives the so called cloud point for the phase transition by condensation in the finite system.

(ii) The existence of an overcritical droplet does not imply sufficiently that the droplet is more stable than the initial vapor phase. This means in terms of the equilibrium probability that in dependence on the initial supersaturation the vapor becomes more probable than the droplet or vice versa. Only for a certain supersaturation y_{coex} the vapor and the droplet have the same probability. For this case the stable droplet radius has to validate eq. (13) and the additional condition: $P^o(1) = P^o(1)$. It leads to the condition for the stationary potential

$$\Phi_s(1) = 0 \qquad (15)$$

because $\Phi_s(1)$ is also equal to zero.
Thus we can calculate y_{coex} from the system of equations (13), (15). For $y > y_{coex}$ the droplet becomes more stable and thus more probable than the initial vapor phase, for $y < y_{coex}$ the vapor possesses the larger equilibrium probability.

(iii) The nucleation barrier becomes smaller and smaller with an increasing supersaturation and the critical droplet size 1_{cr} changes to smaller values too. At a certain value of the supersaturation 1_{cr} comes into the molecular region (only 1 or 2 particles). In this case the nucleation barrier ceases to exist and the nucleation process is converting into a spinodal decomposition. That means the initial stable state becomes unstable instead of metastable and the equilibrium probability of the vapor phase tends to zero.
We can estimate this critical supersaturation by means of eq. (13) if we assume, that in this case the relation $N-1_{cr} \approx N$ is held. The supersaturation for the convertion into spinodal decomposition then is given by

$$y_{sd} = \exp(d_o/r_o) \qquad (16)$$

where r_o is the radius of the molecular size (a few Å).

5. Conclusions

First we give a schematic review of the discussed results by plotting the shapes of $P^o(1)$ for various values of the initial supersaturation (see fig. 2). It shows clearly the close relation between the thermodynamic parameters and the existence of a stable droplet. In fig. 3 the bistable behaviour of the considered system is demonstrated. y gives a measure for the distance from the equilibrium state. In analogy to nonequilibrium chemical systems a new stable state is obtained far from equilibrium. The transition takes place by a nucleation process for $y < y_{sd}$.

References

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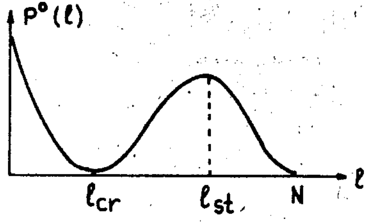

Fig. 1 Equilibrium probability distribution versus cluster size. 1_{st} is the stable droplet size, 1_{cr} the critical droplet size

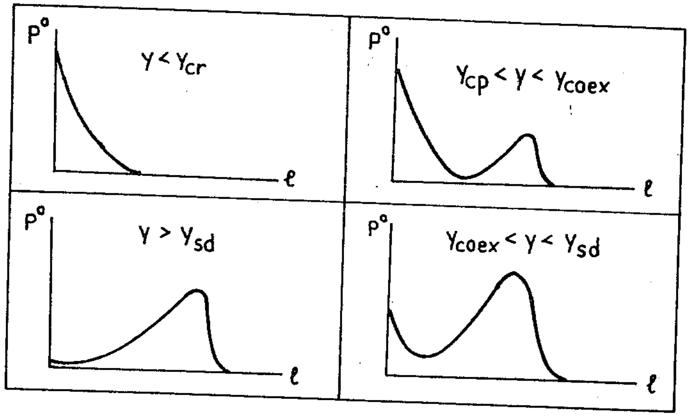

Fig. 2 Schematic plot of the equilibrium distribution in dependence on the initial supersaturation

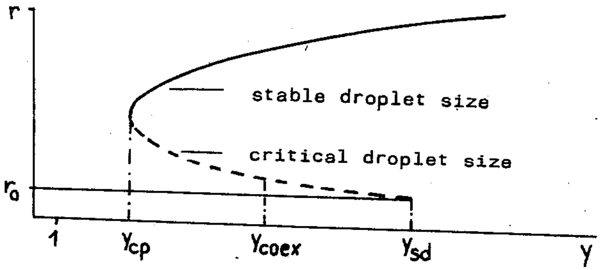

Fig. 3 Stable and critical droplet size as a function of the distance from equilibrium (supersaturation)

Rostocker Physikalische Manuskripte, Heft 9 (1986)

Nichtgleichgewichts-Greensche Funktionen und kinetische Gleichungen

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Anliegen der vorliegenden Arbeit ist die Bereitstellung eines Formalismus zur Nichtgleichgewichts-Beschreibung von Vielteilchensystemen, der die Ableitung von kinetischen Gleichungen auf dem Niveau von Näherungen gestattet, wie sie aus der Behandlung dieser Systeme im thermodynamischen Gleichgewicht bzw. bei T = 0 gut bekannt sind. Das Vorgehen wird am Modell des Elektronengases demonstriert, ist aber für beliebige Systeme durchführbar. Der Hamiltonoperator lautet

$$H = H_o + H_{int} + H_{ext}(t), \tag{1}$$

$$H_o = \int d^3\mathbf{r}\, \Psi^+(\mathbf{r})(-\frac{\hbar^2}{2m}\Delta)\Psi(\mathbf{r}), \tag{2}$$

$$H_{int} = \frac{1}{2}\int d^3\mathbf{r}\, d^3\mathbf{r}'\, \Psi^+(\mathbf{r})\Psi^+(\mathbf{r}')\, v(\mathbf{r}-\mathbf{r}')\, \Psi(\mathbf{r}')\Psi(\mathbf{r}) \tag{3}$$

$$H_{ext}(t) = \int d^3\mathbf{r}\, \varrho_{ext}(\mathbf{r},t)\int d^3\mathbf{r}'\, v(\mathbf{r}-\mathbf{r}')e\, \Psi^+(\mathbf{r}')\Psi(\mathbf{r}') \tag{4}$$

Ψ, Ψ^+ sind Feldoperatoren der Elektronen, von deren Spinabhängigkeit wir hier zur Vereinfachung absehen. Desgleichen soll der spezielle Charakter der Coulomb-Wechselwirkung, also $v(\mathbf{r}) = e^2/|\mathbf{r}-\mathbf{r}'|$, und damit das Problem der Abschirmung nicht betrachtet werden.
Nichtgleichgewicht wird durch extern kontrollierte Ladungen gemäß (4)- und nicht durch Anfangsbedingungen - produziert, und wir interessieren uns für die zeitliche Entwicklung des Systems unter dem Einfluß dieser mechanischen Störung. Da in diesem Sinne der Einfluß von bestimmten Anfangsbedingungen, speziell von -korrelationen, ebenfalls nicht interessiert, wird der Anfangszeitpunkt bei $t_o \longrightarrow -\infty$ gewählt und der statistische Operator $\varrho(-\infty) = \varrho_o$ als unkorreliert angesetzt.
Wie üblich könnte man jetzt kausale Greensche Funktionen (GF) über die Feldoperatoren im Heisenbergbild definieren und nach