NUCLEATION UNDER DIFFERENT BOUNDARY CONDITION[1]

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Based on the canonical ensemble the thermodynamic state function $F(T, V, N)$ in dependence of the cluster distribution N and the thermodynamic parameters (fixed temperature T and volume V) is calculated. Comparing with other situations of different boundary conditions (e.g. fixed energy U in the isoenergetic case) the extrema of the state function in the high dimensional space of independent variables are evaluated.

1. Introduction

The scenario of first-order phase transitions is of great interest in experimental and theoretical disciplines of physics [1]. If we consider a vapour at equilibrium then a certain change of the thermodynamic parameters is able to remove the system into a nonequilibrium state. The vapour becomes supersaturated and a phase transition by homogeneous nucleation can occur in the system.

The basic quantity describing the situation is the cluster distribution N at time t

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

which gives the number of clusters N_n of size n. The free particles (molecules) are called monomers of size $n = 1$. The bound states are clusters of size $n \geq 2$.

Investigating a finite system the overall number of particles is fixed. The boundary condition

$$M_0 = \sum_{n=1}^{N} n N_n = const$$

holds taking into account that the particles are either free or bounded in clusters. Concerning the other thermodynamic boundary conditions we can choose different situations which correspond to the respective thermodynamic potential. The following situations are of interest
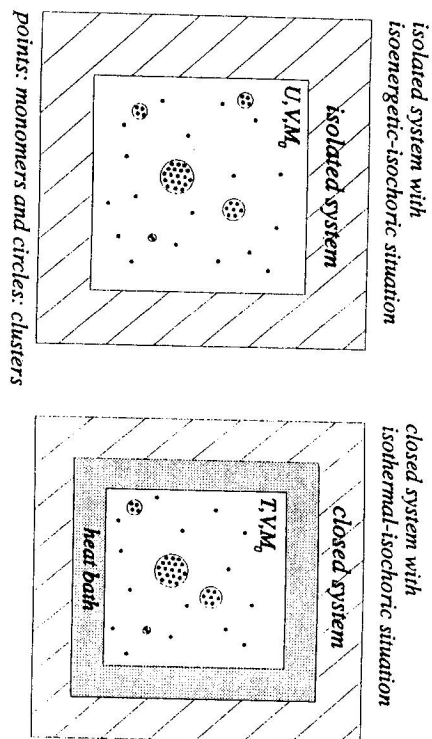
Fig. 1. Isolated (a) and closed (b) systems with isoenergetic-isochoric situation. Points are monomers, circles represent clusters.

- Temperature T, volume V and total particle number M_0 are fixed: Free energy $F(T,V,N)$

- Temperature T, pressure p and total particle number M_0 are fixed: Free enthalpy $G(T,p,N)$

- Inner energy U, volume V and total particle number M_0 are fixed: Entropy $S(U,V,N)$

Figure 1 shows schematically two different situations: the isolated model with fixed energy and changing temperature (left) and the opposite possibility with fixed temperature and changing energy (right).

2. Canonical Ensemble

Our system is given by the cluster distribution $\mathbf{N}$. The total Hamiltonian $H(\mathbf{N})$ reads

$$H = \sum_{n=1}^{N} H_n$$

with the contribution H_n for the N_n clusters of size n at coordinates $\mathbf{r}_i^{(n)}$ and momentum $\mathbf{p}_i^{(n)}$

$$H_n(\mathbf{p}^{(n)}, \mathbf{r}^{(n)}) = \sum_i \frac{\left(p_i^{(n)}\right)^2}{2m_i^{(n)}} + \sum_{i<j} U_{ij}^{(n,n)}(|\mathbf{r}_i - \mathbf{r}_j|)$$

The mass $m_i^{(n)}$ of a cluster containing n monomers is given by

$$m_i^{(n)} \equiv m_n = n\,m$$

where m is the mass of one monomer.

The canonical partition function consists of an ideal part due to the kinetic energy

$$Z_{ideal}(T,V,\mathbf{N}) = \prod_{n=1}^{N} \frac{V^{N_n}}{N_n! h^{3N_n}} \left(\sqrt{2\pi m_n kT}\right)^{3N_n}$$

and a second term $Z_{binding}(T,V,\mathbf{N})$ due to the energy stored in the cluster. Both terms together read

$$Z(T,V,\mathbf{N}) = \prod_{n=1}^{N} \frac{V^{N_n}}{N_n!} \left[\left(\frac{\sqrt{2\pi m_n kT}}{h}\right)^3 \exp\left(-\frac{f_n}{kT}\right) \right]^{N_n}$$

where the binding energy $f_n(T)$ is the minimum value of the potential energy averaged over all spatial arrangements of the n bounded monomers

$$f_n(T) = \min_{\mathbf{r}} \sum_{i<j} U_{ij}^{(n,n)}(|\mathbf{r}_i - \mathbf{r}_j|).$$

From the canonical partition function we can calculate the thermodynamic quantities using the relation

$$F(T,V,\mathbf{N}) = -kT \ln Z(T,V,\mathbf{N}).$$

3. Isothermal-Isochoric Situation

State function: Free energy $F(T,V,\mathbf{N})$

$$F(T,V,\mathbf{N}) = kT \sum_{n=1}^{N} N_n \left[\ln(\lambda_n(T)^3 N_n/V) - 1\right] + \sum_{n=1}^{N} N_n f_n(T)$$

with $\lambda_n(T) = n^{-1/2}\lambda_1(T) = n^{-1/2}\left(h^2/(2\pi m kT)\right)^{1/2}$. By derivation of the state function we get the following quantities:

- Pressure

$$p(T,V,\mathbf{N}) = -(\partial F/\partial V)|_{V,\mathbf{N}} = kTN_0/V$$

with $N_0 = \sum_{n=1}^{N} N_n$,

- Entropy

$$S(T,V,\mathbf{N}) = -\left(\frac{\partial F}{\partial T}\right)\Big|_{V,\mathbf{N}} = k\sum_{n=1}^{N} N_n \left[\frac{5}{2} - \ln\left(\frac{\lambda_n(T)^3 N_n}{V}\right)\right] - \sum_{n=1}^{N} N_n \frac{\partial f_n(T)}{\partial T}$$

- Chemical potential

$$\mu_n(T,V,\mathbf{N}) = (\partial F/\partial N_n)|_{T,V,N\neq N_n} = kT\ln(\Lambda_n(T)^3 N_n/V) + f_n(T)$$

- Internal energy

$$U(T,V,\mathbf{N}) = F(T,V,\mathbf{N}) + TS(T,V,\mathbf{N})$$
$$= \frac{3}{2}kTN_0 + \sum_{n=1}^{N} N_n\left[f_n(T) - T\frac{\partial f_n(T)}{\partial T}\right]$$

- Free enthalpy

$$
\begin{aligned}
G(T,V,\mathbf{N}) &= F(T,V,\mathbf{N}) + Vp(T,V,\mathbf{N}) \\
&= U(T,V,\mathbf{N}) - TS(T,V,\mathbf{N}) + Vp(T,V,\mathbf{N}) \\
&= kT\sum_{n=1}^{N} N_n\ln(\Lambda_n(T)^3 N_n/V) + \sum_{n=1}^{N} N_n f_n(T) \\
&= \sum_{n=1}^{N} N_n \mu_n(T,V,\mathbf{N})
\end{aligned}
$$

- Enthalpy

$$H(T,V,\mathbf{N}) = U(T,V,\mathbf{N}) + Vp(T,V,\mathbf{N}) = \frac{5}{2}kTN_0 + \sum_{n=1}^{N} N_n\left[f_n(T) - T\frac{\partial f_n(T)}{\partial T}\right]$$

- Specific heat

$$
\begin{aligned}
c_V(T,V,\mathbf{N}) &= (\partial U/\partial T)|_{V,\mathbf{N}} = -T(\partial^2 F/\partial T^2)|_{V,\mathbf{N}} \\
&= T(\partial S/\partial T)|_{V,\mathbf{N}} = \frac{3}{2}kN_0 - T\sum_{n=1}^{N} N_n\frac{\partial^2 f_n(T)}{\partial T^2}
\end{aligned}
$$

4. Isothermal–Isobaric Situation

State function: Free enthalpy $G(T,p,\mathbf{N})$ From $G(T,V,\mathbf{N}) = F(T,V,\mathbf{N}) + Vp(T,V,\mathbf{N})$ follows with $V(T,p,\mathbf{N}) = kTN_0/p$ $G(T,p,\mathbf{N}) = F(T,V(T,p,\mathbf{N}),\mathbf{N}) + pV(T,p,\mathbf{N})$, and the final state function reads

$$G(T,p,\mathbf{N}) = kT\sum_{n=1}^{N} N_n\ln\left(\frac{\Lambda_n(T)^3 N_n p}{kTN_0}\right) + \sum_{n=1}^{N} N_n f_n(T)$$

with $\Lambda_n(T) = n^{-1/2}\Lambda_1(T) = n^{-1/2}\left(h^2/(2\pi m kT)\right)^{1/2}$ and $N_0 = \sum_{n=1}^{N} N_n$. After derivation we get

- Volume

$$V(T,p,\mathbf{N}) = -(\partial G/\partial p)|_{T,\mathbf{N}} = kTN_0/p$$

- Entropy

$$
\begin{aligned}
S(T,p,\mathbf{N}) &= -(\partial G/\partial T)|_{p,\mathbf{N}} \\
&= k\sum_{n=1}^{N} N_n\left[\frac{5}{2} - \ln\left(\frac{\Lambda_n(T)^3 N_n p}{kTN_0}\right)\right] - \sum_{n=1}^{N} N_n\frac{\partial f_n(T)}{\partial T}
\end{aligned}
$$

- Chemical potential

$$
\begin{aligned}
\mu_n(T,p,\mathbf{N}) &= (\partial G/\partial N_n)|_{T,p,N\neq N_n} \\
&= kT\left[\ln\left(\frac{\Lambda_n(T)^3 N_n p}{kTN_0}\right) + 1 - \frac{N_n}{N_0}\right] + f_n(T)
\end{aligned}
$$

- Internal energy

$$
\begin{aligned}
U(T,p,\mathbf{N}) &= G(T,p,\mathbf{N}) + TS(T,p,\mathbf{N}) - pV(T,p,\mathbf{N}) \\
&= \frac{3}{2}kTN_0 + \sum_{n=1}^{N} N_n\left[f_n(T) - T\frac{\partial f_n(T)}{\partial T}\right]
\end{aligned}
$$

- Free energy

$$
\begin{aligned}
F(T,p,\mathbf{N}) &= G(T,p,\mathbf{N}) - pV(T,p,\mathbf{N}) \\
&= kT\sum_{n=1}^{N} N_n\left[\ln\left(\frac{\Lambda_n(T)^3 N_n p}{kTN_0}\right) - 1\right] + \sum_{n=1}^{N} N_n f_n(T)
\end{aligned}
$$

- Enthalpy

$$
\begin{aligned}
H(T,p,\mathbf{N}) &= U(T,V,\mathbf{N}) + pV(T,p,\mathbf{N}) \\
&= \frac{5}{2}kTN_0 + \sum_{n=1}^{N} N_n\left[f_n(T) - T\frac{\partial f_n(T)}{\partial T}\right]
\end{aligned}
$$

- Specific heat

$$
\begin{aligned}
c_p(T,p,\mathbf{N}) &= (\partial H/\partial T)|_{p,\mathbf{N}} = -T(\partial^2 G/\partial T^2)|_{p,\mathbf{N}} \\
&= T(\partial S/\partial T)|_{p,\mathbf{N}} = \frac{5}{2}kN_0 - T\sum_{n=1}^{N} N_n\frac{\partial^2 f_n(T)}{\partial T^2}
\end{aligned}
$$

5. Temperature Dependencies

The negative binding energies $f_n(T)$ for each cluster size have to be introduced empirically. Using the well-known Bethe–Weizsäcker ansatz

$$f_n(T) = \mu_\infty(T) n + \sigma A_n$$

with the surface of a size-n-cluster

$$A_n = (c_\alpha 4\pi/3)^{-3/2} n^{2/3}$$

indicating volume and surface contributions we take this formula valid for cluster sizes $n \geq 2$ and $f_1(T) = 0$ for isolated monomers.
The chemical potential of a monomer over a flat surface is

$$\mu_\infty(T) = kT \ln\left(\lambda_1(T)^3 c_{eq}(T)\right)$$

The equilibrium concentration $c_{eq}(T)$ is connected with the equilibrium vapour pressure $p_{eq}(T)$ by the ideal gas law

$$c_{eq}(T) = \frac{p_{eq}(T)}{kT}$$

Therefore we get the following temperature derivative

$$\frac{\partial f_n}{\partial T} = k \left[\frac{\mu_\infty + \Delta Q}{kT} - \frac{5}{2} \right] n$$

6. Isoenergetic-Isochoric Situation

State Function: Entropy $S(U, V, \mathbf{N})$. From the caloric state equation $U = U(T, V, \mathbf{N})$ we get by transformation $T = T(U, V, \mathbf{N})$ which has to be inserted in $S(T, V, \mathbf{N})$ to find the final state function $S(U, V, \mathbf{N})$.

$$S(U, V, \mathbf{N})/k = \left[\frac{3}{2} N_0 + \frac{5}{2} M_\alpha\right] \ln\left(\frac{U - \sigma A_\alpha + \Delta Q M_\alpha}{kT_0(3N_0/2 + 5M_\alpha/2)}\right)$$
$$+ \frac{5}{2} N_0 + \left[\frac{5}{2} - \ln\left(\lambda_1(T_0)^3 c_0\right) - \frac{\Delta Q}{kT_0}\right] M_\alpha$$
$$- \sum_{n=1}^N N_n \ln\left(\lambda_n(T_0)^3 N_n/V\right)$$

with the initial temperature

$$T_0 = \frac{2U_0}{3k M_0}$$

The abbreviations are the total number of clusters including monomers
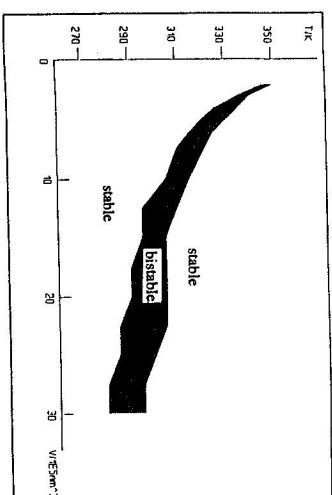
$$N_0 = \sum_{n=1}^N N_n,$$

Fig. 2. Area bistability with the thermodynamic function $S = S(U, V, N)$ (the inner energy U is replaced by T).

the total cluster surface

$$A_\alpha = \sum_{n=2}^N A_n N_n$$

and the total number of monomers bounded in clusters

$$M_\alpha = \sum_{n=2}^N n N_n.$$

7. Results

In the framework of thermodynamics the question of nucleation is connected with the calculation of extrema of the thermodynamic potential. The search of these states of stable or unstable equilibrium, for example of the free energy $F = F(T, V, \mathbf{N})$, can be done by changing the cluster distribution $\mathbf{N}$ via reactive collisions. The monomer–cluster–reactions $N_1 + N_n \Longleftrightarrow N_{n+1}$ (formation and dissolution of clusters by one monomer) are the most important reaction channels.

Starting with M_0 monomers the system looks like a gas or vapour as the one-phase-state. The vapour is changed to a supersaturated state by quenching (undercooling). Just at that moment the system is in a metastable state. This is our initial situation. By nucleation in the forming of clusters the system changes to a two-phase-state, where the liquid (one big cluster) is in equilibrium with the surrounding gas. The state of equilibrium in this system corresponds to the minimum of the free energy function

$$F(T, V, \mathbf{N}) = kT \sum_{n=1}^N N_n \left[\ln\left(\lambda_n(T)^3 N_n/V\right) - 1\right] + \sum_{n=1}^N N_n f_n(T)$$

with

$$f_n = \mu_\infty(T) n + \sigma A_n.$$

The temperature T, the volume V and the total particle number M_0 are fixed. We get the following results:

- $V = 1.9 \cdot 10^{-21} \text{ m}^3$

- $M_0 = 15000$ particles

temperature [K]	equilibrium distribution		free energy
293	$N_1 = 1388$ and $N_{13612} = 1$		$F = -275913.52 \, kT$
300	$N_1 = 2185$ and $N_{12815} = 1$		$F = -270537.35 \, kT$

These considerations are possible for the entropy $S = S(U, V, \mathbf{N})$ too.

Figure 2 shows the area of bistability where the thermodynamic function has two extrema which correspond to the only–small–clusters–situation and the one–big–droplet–situation. In dependence of the boundary conditions the monostable case without nucleation to the new cluster state is more probable.

8. Conclusions

To study the dynamics of the nucleation process it is necessary to investigate the landscape of the thermodynamic state function, e.g. entropy, in the high dimensional space of independent variables (inner energy U, volume V, cluster distribution $\mathbf{N}$). The maximum of $S(U, V, \mathbf{N})$ corresponds to the equilibrium situation. In some region of the U–V–M_0–space we find two maxima of S divided by a saddle point (bistability). One distribution $\mathbf{N}^{(1)}$ consists of a number of small clusters (vapour phase), the other distribution $\mathbf{N}^{(2)}$ consists of one big cluster accompanied by few small clusters (liquid phase).

References

[1] C. Domb; M.S. Green; J.L. Lebowitz: Phase Transitions and Critical Phenomena, Vol. 1 – 11, Academic Press, London, New York, 1972 – 1987

[2] H. Ulbricht; J. Schmelzer; R. Mahnke; F. Schweitzer: Thermodynamics of Finite Systems and the Kinetics of First–Order Phase Transitions, Teubner–Texte zur Physik, Vol. 17, Teubner–Verlag, Leipzig, 1988

[3] R. Mahnke, A. Budde: Pattern Formation by Cellular Automata, Syst. Anal. Model. Simul. (SAMS) 10 (1992) 133