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STATISTICAL DESCRIPTION OF THE METASTABLE STATE

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STATISTICAL DESCRIPTION OF THE METASTABLE STATE

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Abstract

The statistical ensemble for metastable state is proposed, that define the statistical and thermodynamical properties of the metastable system. The proposed ensemble gives the initial conditions for the kinetic problems of the first order phase transition theory.

In the equilibrium state the probability distribution for a system is the Gibbs distribution

$$W = \exp\left(\frac{F-H}{T}\right) \qquad (1)$$

H being the Hamiltonian of the system, T - the temperature and F - the thermodynamical potential.

In the discontinuous phase transition the equilibrium state changes from the macroscopicaly homogeneous to the inhomogeneous. In that inhomogeneous state the system contains a region of the new phase with space size larger than R_c, R_c being the critical nucleus size. The probability of a microscopical state is given by (1), and the probability of every macroscopically homogeneous state is negligibly small. By special technuques one is able to obtain the metastable homogeneous state, which is the continuation of the homogeneous state the system had before the phase transition. The aim of this paper is to propose the statistical ensemble for the metastable phase. Let $\varphi(x)$ be the parameters), that describe the change of the state in the phase transition. For the liquid - vapor phase transition φ is the particle density. The ensemble for the metastable state has to give the relative probability for homogeneous states as close as possible to those of the Gibbs ensemble (1), but the probability of inhomogeneous states should be as small as in the equilibrium state before the phase transition. To construct such an ensemble, we exploit the assumed property of the equilibrium in homogeneous state, that the size of the new phase region is larger than R_c for that state, and the fluctuation, in which nucleus of a size λ, $\lambda \ll R_c$, appears is as rare as in the homogeneous phase. The correlation radius r_c for the fluctuations of $\varphi(x)$ is expected to be finite in the vicinity of the first order phase transition point. The critical nucleus size R_c is at this point infinite, and in the vicinity of this point $R_c \gg r_c$. Let us divide the system into cells of a size λ, $R_c \gg \lambda \gg r_c$. The volume of a cell is $V(\lambda)$. For the cell number i we introduce the quantity $\Phi_i(\lambda)$

$$\Phi_i(\lambda) = \int \varphi(x)\,dx\,, \quad x \in V_i(\lambda). \qquad (2)$$

The average values of $\varphi(x)$ for the two homogeneous phases and for corresponding metastable states we denote as φ_1 and φ_2 , $\varphi_2 > \varphi_1$. The probability of values of $\Phi_i(\lambda) = V(\lambda)\varphi_0$ in this homogeneous states is expected to be small for $\varphi_1+\Delta_1 < \varphi_0 < \varphi_2-\Delta_2$, $\Delta_{1,2} > \Delta_0 \sim [V(\lambda)]^{-1/2}$. Let us chose such a value φ_0 and $\Phi_0 = V(\lambda)\varphi_0$ with negligible small probability of appearance in a cell. The distribution we propose for two metastable states, connected with phases 1 and 2, is

$$W^{\pm} = exp\left(\frac{F-H}{T}\right)\prod_i \Theta[\pm(\Phi_0-\Phi_i(x))], \tag{3}$$

the Θ - function is $\Theta(y) = 1$, $y \leq 0$, and $\Theta(y)=0$ $y>0$. To bring (3) in a more convenient form, one have to introduce the function $P(y) = \ln\Theta(y)$. From (3) one has (in our case $P(y) = TP(y)$)

$$W^{\pm} = exp\left(\frac{F-\tilde{H}^{\pm}}{T}\right), \tag{4}$$

$$\tilde{H}^{\pm} = H - \sum_i P[\pm(\Phi_0 - \Phi_i(\lambda))]. \tag{5}$$

To exclude the fixed cell lattice, let us use the function $J(x)$, $J(x)=1$, $0 \leq x \leq 1$; $J(x)=0$, $x \in]-\infty,0[,]1,\infty[$. Instead of (5) we have

$$\tilde{H}^{\pm} = H - \int dx\, P\{\pm\int J(\lambda^{-1}|x-x'|)[\varphi_0-\varphi(x')]\,dx'\} \tag{6}$$

For computations it is convenient to take advantage of a re - presentation of the θ - function as a limit of a continuous function ~~as a limit of a continuous function~~, for example

$$\Theta(y) = \lim_{\gamma\to\infty}\frac{1+th(\gamma y)}{2},$$

$$P(y) = \lim_{\gamma\to\infty}\ln\frac{1+th(\gamma y)}{2}. \tag{7}$$

For (4) and (6) one obtains

$$W^{\pm} = \lim_{\gamma\to\infty} W_\gamma^{\pm};\quad W_\gamma^{\pm} = exp\left\{\frac{F-\tilde{H}_\gamma^{\pm}}{T}\right\}, \tag{8}$$

$$\tilde{H}_\gamma^{\pm} = H - \int dx\, \ln\{1 \pm th[\gamma\int J(\lambda^{-1}|x-x'|)[\varphi_0-\varphi(x')]dx']\}, \tag{9}$$

the constant term is included in the energy F. The thermodyna-

mics of the metastable system is based, in the usual way, on the thermodynamical energy F

$$F^{\pm} = -T\ln\tilde{Z}^{\pm};\quad \tilde{Z}^{\pm} = \sum exp\left(-\frac{\tilde{H}^{\pm}}{T}\right). \tag{10}$$

the sum in (10) is carried out over all states of the system. For the distribution $W_\gamma^{\pm}$ the probability of a cell with the new phase is of the order of $\xi_\gamma = exp[\gamma V(\lambda)|\varphi_0-\varphi_{1,2}|]$ and it is possible to use a constant value of $\gamma \gg \gamma_0$, instead of the $\gamma\to\infty$ limit,

$$\gamma_0 = [V(\lambda)|\varphi_0-\varphi_{1,2}|]^{-1}. \tag{11}$$

By using the ensemble (4), (6) instead of the Gibbs en - semble (1) one has a small change in properties of the system. The change is of relative order of $\xi = exp(-V(\lambda)\Delta f)$, Δf being the increase of the energy per unit volume for a process of changing φ from $\varphi_{1,2}$ to φ_0 . For λ = const, there is no singularity in the energy, F at the transition point. The limit $\lambda\to\infty$ is to take, for the metastable state, after the limit T $\longrightarrow$ T_0, T_0 being the transition temperature.

The system in metastable state is stable with respect to small perturbations of a large space size $L \gg R_c$. When moving into the metastable region one can reach the spinodal line, at which this stability is lost. At the spinodal line the susceptibility $\chi=\infty$, $\chi = \frac{\partial^2 F}{\partial h^2}$, h being the field, thermodynamicaly conjugated to φ , and the correlation function $G(p)$,

$$G(p) = \int G(x)e^{ipx}dx,\quad G(x-x') = \langle\varphi(x)\varphi(x')\rangle - \langle\varphi\rangle^2, \tag{12}$$

becomes infinite for $p\to 0$. Both F and G are defined in the ensemble (4), (5). The condition for the spinodal line

$$G^{-1}(0) = 0 \tag{13}$$

is possible to wright, using, for example, Matzubara Green--functions method.

Essential problems in the discontinuous (first oder) phase transition theory are the thermodynamics and statistics of the metastable state and the dynamics of the metastable system. The statistical operator (4), (6) gives the thermodynamics and statistics. The dynamics is described, when the equation of motion

$$-i\hbar \frac{\partial W(t)}{\partial t} = [HW - WH]$$

is solved under the initial condition $W(0) = W^{\pm}$. In phenomenological theory the equation of motion may be chosen in the appropriate way; distribution (4), (6) gives the initial condition for the relaxing distribution function.

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