First direct confirmation of nano-nucleation and new nucleation theory

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Abstract:

Crystallization from the melt or gas is one of the most popular and well-known phenomena in any materials. Nucleation which is the early process of crystallization controls significantly structure and physical properties. Although classical nucleation theory (CNT) assumed theoretically the nucleation in the 1930s, nobody could succeed in confirming the nucleation because of technical difficulties.

We succeeded in experimental confirmation of nucleation of nano-nuclei of polyethylene (PE) for the first time by means of small angle X-ray scattering (SAXS). We obtained evolution of the size distribution of nuclei $f(N,t)$ from the order of nano to sub-micron meters, where N is number of repeating unit in a nucleus and t is crystallization time. It clarified the real image of nucleation that nano-nucleus shows significant fluctuation in size and shape and repeats frequent generation and disappearance, while macroscopic crystal shows little fluctuation.

CNT proposed so called fundamental kinetic equation with respect to $f(N,t)$ in nucleation process assuming the nucleation process as a linear sequential rate process. It has been long believed that the kinetic equation can describe the nucleation process correctly. However we found that the kinetic equation in CNT does not satisfy the mass conservation law. We proposed a new nucleation theory by introducing a "mass distribution function $Q(N,t) \propto Nf(N,t)$". And we proposed a new basic equation of the mass conservation law, $\partial Q(N,t)/\partial t = -\partial \boldsymbol{j}(N,t)/\partial N$, where $\boldsymbol{j}(N,t)$ is net flow. This solved the above problem in CNT. We obtained $Q(N,t)$ by means of SAXS and verified the new nucleation theory.