

Equilibrium drops and their effect on classical and statistical thermodynamics

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Abstract

In 2010, liquid equilibrium drops were discovered by methods of statistical thermodynamics. The concept of the «equilibrium» means that there is a strict equilibrium between the droplet and surrounding vapor including three partial equilibria: mechanical, thermal and chemical. The latter conditions for the phase equilibrium have been derived by Gibbs for macroscopic phases. That is, in these equilibrium drops at isothermal conditions ($T=const$) there are realized equalities for internal pressure of vapor and liquid $P_\alpha = P_\beta$, and also equality of chemical potentials $\mu_\alpha = \mu_\beta$, here α and β are symbols of the coexisting phases. Because of the equality $P_\alpha = P_\beta$, the equilibrium drops principally differ from traditional metastable drops showing a rupture of internal pressure between vapor and liquid, $P_\alpha = P_\beta + 2\sigma/R$, due to an interface possessing a surface tension σ of spherical drops of radius R . Therefore, the equilibrium drops could not be realized in classical thermodynamics. In another words, a discovery of the equilibrium drops indicates a basic error in classical thermodynamics for the surface phenomena and small systems as well as in all the statistical theories of the curved interface derived on the basis of the classical thermodynamics. It has been found out later that the above error is linked with improper usage of experimental data on characteristic relaxation times of momentum transfer τ_P , mass transfer τ_μ , and heat energy transfer τ_T . In the general case, the following relationships are hold: $\tau_p \ll \tau_T \ll \tau_\mu$, however nowadays, the classical and statistical thermodynamics of curved interfaces uses assumption $\tau_P \gg \tau_T$. The correct accounting for $\tau_p \ll \tau_T$ has clarified the following results.

For classical thermodynamics:

It has been shown a redundancy of the theory offered by Caratheodory for a substantiation of use integrating factor in order to consider entropy as a function of state.

The microscopic analysis of the Second Law of Thermodynamics has allowed one to explain an essence of two processes: in the first, the entropy S formation from t_0 to t_s takes place; and in the second one occurring after t_s , the entropy S_t Production does. Moreover, it has explained a ratio $S_t < S_{eq}$.

Statistical thermodynamics:

There have been clarified principles how to introduce the coarse-grained spatial description of kinetic equations for non-equilibrium systems. As well, there have been validated two expressions for Maxwell-Boltzmann distribution function at various time scales.

It has been introduced a general definition of a surface tension (ST) for any curved interfaces. It has been explained two Gibbs ST definitions for equilibrium. The surface formation due to mechanical perturbations is nonequilibrium or dynamic ST. It has been shown a complex nature of Young's equation. It has been shown a necessity to include connected states of molecules in associations with their anharmonic oscillations because of it changes equations of non-ideal gases and liquids theories. Kinetic models must be self-consistent, i.e. an equality of direct and reverse reaction rates must give the same equilibrium constants as those constructed in the framework of equilibrium distribution. The same principle is of importance for equilibrium and dynamics of phase transitions.

Biography

Tovbin Yu.K has completed his PhD at 1974 and Ph. Sci. at 1985 from Karpov Scientific Research Institute of Physical Chemistry (KSRIIP), Moscow. He was the Prof. and Head of Laboratory KSRIIP (up to 2018). He is the expert in the field of statistical thermodynamics. He is the author of three monographies and more than 350 publications, including: Tovbin Yu.K., Theory of physical chemistry processes at a gas-solid surface processes, CRC Press, Boca Raton, FL, 1991; Tovbin Yu.K. Lattice- Gas Model in Kinetic Theory of Gas – Solid Interface Processes // Progress in Surface Science. 1990. V. 34. № 1-4. P. 1 - 235. Tovbin Yu.K., Molecular theory of adsorption in porous solids, CRC Press, Boca Raton, FL, 2017; Tovbin Yu.K., Small systems and fundamentals of thermodynamics, CRC Press, Boca Raton, FL, 2018. Tovbin Yu. K., Second Law of Thermodynamics, Gibbs' Thermodynamics, and Relaxation Times of Thermodynamic Parameters // Russian Journal of Physical Chemistry A, 2021, Vol. 95, No. 4, pp. 637–658.

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