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The Comparative Analysis of the different thermodynamical methods for the determination of the fluid phase stability boundary

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The stability boundary of the homogeneous phase is closely connected with its equation of state. Any equation of state, supposed to be valid from the point of view of physics rather than just be an interpolation formula, should be created with regard to the spinodal. The development of such equation and finding the stability boundary is the most reliable and correct way of determining the spinodal.

In order to determine the spinodal we can use the unified equations of state and even the simple equations of the Van–der-Wals type, for example, the equation of Himpan.

$$[\pi + f_a(\varphi - f_b) (\varphi \cdot \tau - f_c)] \cdot (\varphi - f_d) = s \cdot \tau.$$

Here $\pi = P/P_c$, $\varphi = V/V_c$, $\tau = T/T_c$. are the transformed pressure, volume and temperature.

The PT isochores are rectilinear, from which follows the linear dependence of the derivative $(\delta P / \delta V)_T$ and the inverse value of compressibility β_T^{-1} on temperature and pressure (along the isochores). In fact, if the equation of state is

$$P = [T - T_c(V)] \cdot (\delta T / \delta P)_{V,S},$$

where $T_c(v)$ and $(\delta T \delta P)_{v,s}$ are the functions of the specific volume only, then the derivative $(\delta P \delta V)_T$ along the isochore will be the linear function of pressure and temperature.

Thus, in order to find the spinodal coordinates, one can use the linear extrapolation to zero with respect to the isochore derivative $(\delta P \delta V)_T$ or β_T^{-1} .

Until recently only the thermal data was used to find the homogeneous phase stability boundary. However, the development of procedures connected to the extrapolation of other thermophysical magnitudes is of great importance for the evaluation of the spinodal calculation techniques precision. It is not difficult to demonstrate the linear dependence of the $T/(C_P - C_V)$ complex on temperature and pressure on the isochores. Since this complex turns to zero at the spinodal, the spinodal coordinates again come to be its linear extrapolation with respect to temperature and pressure along the isochores.

All spinodal calculation techniques give very satisfactory results. In case of n-hexane the spinodal pressures calculated with the special equation for the metastable area, with the equation of state, with the equation of Himpan and Furt, differ only by 1-3 bars, which corresponds to the temperature discordance less than 1K. In case of the specific volume values on spinodal this discordance doesn't exceed 2-3%. For other fluids (water, helium, argon, etc) this discordance is in the same range.

Figure 1 (a, b) presents the results of spinodal calculation with the different techniques. Fluid argon spinodal is obtained from the equation of state for the metastable area, isothermic compressibility extrapolation and heat capacity difference. The results differ by 0.005–0.01 with respect to the transformed temperature (for argon it corresponds to 1.0÷1.5 K) and by 2–3% with respect to the specific volume.

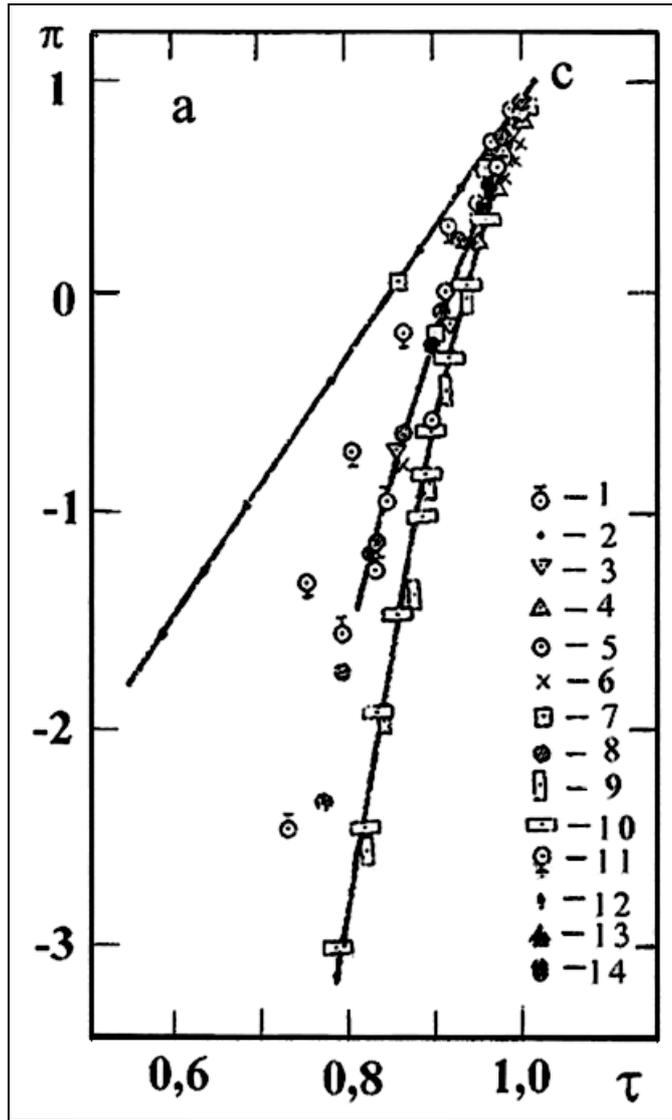
The fluid nitrogen stability boundary is found from the isobaric heat capacity and heat capacity difference extrapolation. The discordance is about 3% with respect to the specific volume.

The fluid helium heat capacity difference extrapolation technique with respect to the unified equation of state gives the discordance of about 1.5% with respect to temperature and less than 2% with respect to volume.

The discordance observed when comparing different calculation techniques is quite compatible with the calculation error but at the same time it characterizes the coordination degree of the techniques in question. Thus, the fluid phase stability boundary cannot be found with more precision than 0.5–1.0% with respect to temperature and 2–3% with respect to specific volume.

The stability boundary is less definite in case of the supersaturated vapor.

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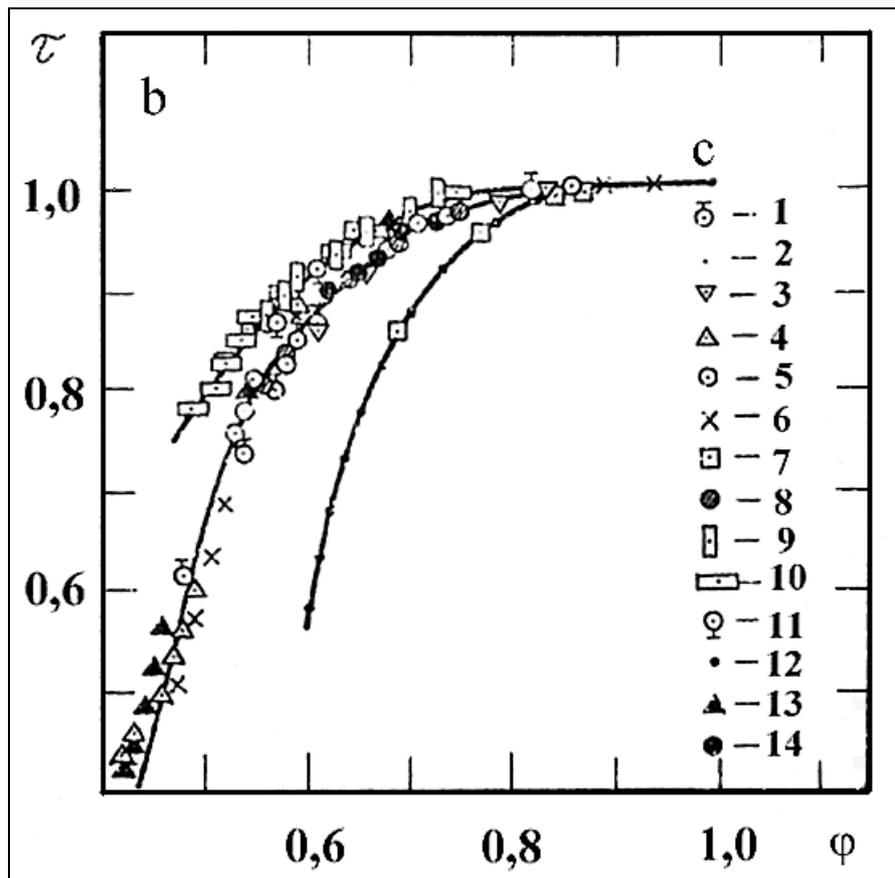


Figure captions

Figure 1

The results of spinodal determination obtained by the different techniques: a – projection $\pi - \tau$; b - $\tau - \varphi$: ($\pi = P/P_{c}$, $\varphi = V/V_{c}$, $\tau = T/T_{c}$ – transformed pressure, volume and temperature; P_{c} , V_{c} , T_{c} – critical parameters); isobaric and isochoric heat capacity extrapolation technique: 1 – argon; 2 – methane, 3 – oxygen; 4 – nitrogen; 5 – ethane; 6 – carbon dioxide; 7 – helium; equation of state for metastable area: 8 – argon; 9 – diethyl ether; 10 – n-hexane; 11 – water; unified equation of state – 12 – helium; compressibility extrapolation: 13 – argon; isobaric heat capacity extrapolation: 14 – nitrogen.