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Questions and Answers

Answer to Professor Tykodi's Question on "A Global Thermodynamic Inequality"

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Professor Tykodi's "global thermodynamic inequality"[1] is violated for any pure substance which exhibits a gas–liquid critical point. The proposed "theorem" may be expressed in the form

$$\{V^{\alpha} - (T^{\alpha} - T^{\beta})(\partial V/\partial T)_P^{\alpha}\} > 0 \tag{1}$$

where the states α, β have the same pressure but different temperatures, and the line segment $[\alpha, \beta] \equiv [(T^{\alpha}, P), (T^{\beta}, P)]$ does not intersect a first-order phase transition line.

Consider pairs of states with $T^{\beta} < T^{\alpha}$ and $T^{\alpha} - T^{\beta} = \Delta T$, a fixed temperature interval, and with $P^{\alpha} = P^{\beta} = P^{c}$, the critical pressure. Let T^{α} be less than T^{c}, so that the line segment $[(T^{\beta}, P); (T^{\alpha}, P)]$ does not cross either the gas–liquid transition curve or its extension, the critical isochore. Now, consider the behavior of the left-hand side of Eq. (1) as T^{α} approaches T^{c}.

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The volume V^{α} approaches the (finite) critical volume V^{c}. As the critical point is approached, the derivative $(\partial V/\partial T)_P$ diverges to plus infinity proportionally to the isothermal compressibility. This is true for classical equations of state, such as the van der Waals equation, as well as for real fluids which exhibit nonclassical critical behavior much discussed in recent years.[2] For pairs of states with α sufficiently close to the critical point, the (negative) second term in Eq. (1) will dominate the first, and the entire expression on the left will be negative. Indeed, the left-hand side of Eq. (1) will diverge to $-\infty$ as $T^{\alpha} \to T^{c}$!

On p. 60 of the textbook referred to in his communication, Tykodi states, "Now it is clear that the..." [left-hand side of Eq. (1)] "...will be positive for states such that $T_{\beta} < T_{\alpha}$ ... ." It is interesting that this assertion is violated for a substance as common and important as water. There exists a region in the PT phase diagram for water[3] extending from the triple point up to about 270 atm (well above $P_c \approx 220$ atm), and over a narrow range of temperatures above the melting temperature $T_m(P)$, in which the coefficient of thermal expansion is negative. For any pressure above the critical pressure of water, but below 270 atm, let α be a state in the region where $(\partial V/\partial T)_P < 0$ and let T^{β} be very much larger than T^{α}. Because we are above the critical pressure, there is no danger that the segment $[\alpha, \beta]$ will intersect the gas–liquid transition curve, so that T^{β} may be chosen as large as necessary to make the left-hand side of (1) negative.

REFERENCES

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3. J. Kestin, *A Course in Thermodynamics*, Blaisdell (1966), pp. 298–302 and references therein.