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METHOD FOR CALCULATING THE STABILITY BOUNDARY (SPINODAL) OF A HOMOGENEOUS STATE OF A MATERIAL

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A method is developed for calculating the stability limit of a homogeneous state of a material based on isochoric heat-capacity measurements.

It was shown in [1] that the behavior of isochoric heat capacity can be described over a wide range of state parameters including the critical region by an equation of the form

$$C_V^*(\varphi,\ \tau) = A_s\left|1 - A_2(\varphi)\,\tau\right|^{-\alpha} + \text{regulation terms.} \tag{1}$$

Equation (1) generalizes the power law of scale theory for noncritical isochores, and compared to traditional methods of C_V calculation has the advantage that it correctly describes C_V behavior in the metastable region and near the stability boundary of the homogeneous state (spinodal). In fact, it follows from Eq. (1) that for $\tau_s(\varphi)$ satisfying the condition

$$A_2(\varphi)\,\tau_s - 1 = 0, \tag{2}$$

the isochoric heat capacity increases without limit. This has been well confirmed by experimental [2-5], numerical [6, 7], and theoretical [8-12] studies. From Eq. (2) we have

$$\tau_s(\varphi) = A_2^{-1}(\varphi), \tag{3}$$

from which follows the physical meaning of the regulation terms of Eq. (1). Consequently, $A_2(\varphi)$ defines the geometric location of singular points on the thermodynamic surface. For each isochor there exists a temperature $\tau_s(\varphi)$ satisfying the condition $\tau_s(\varphi) \leqslant \tau_c(\varphi)$ (this condition follows from the properties of the function $A_2(\varphi)$ studied in [1]), at which C_V increases without limit. Knowing the value of the regulated parameter of $A_2(\varphi)$ for each isochor, Eq. (3) may be used to calculate the temperature at which C_V diverges. Thus these values of τ_s and φ define the position of the spinodal curve.

Table 1 presents values of temperature and density on the saturation line and spinodal curve, calculated from C_V data for a number of n-alkanes [13, 14]. Table 2 compares spinodal

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TABLE 1. Density and Temperature Values on Spinodal Curve, Calculated from C_V Measurements [13, 14] of Several n-Alkanes

ρ', kg/m³	T'_c, K	T'_s, K	ρ'', kg/m³	T''_c, K	T''_s, K
		Methane			
162,00	190,55	190,55	162,00	190,55	190,55
182,02	190	189,38	103,90	190	187,08
199,52	189	188,54	87,11	189	183,46
212,31	188	187,56	81,17	188	181,76
222,52	187	186,65	76,28	187	180,18
231,70	186	184,75	72,05	186	178,68
239,98	185	182,56	68,31	185	177,23
247,52	184	180,25	64,98	184	175,86
254,45	183	177,73	61,99	183	174,56
		Ethane			
299,6	300,55	283,69	201,9	305,33	305,01
322,9	296,66	265,80	176,8	305,16	304,83
341,17	292,479	247,44	148,7	304,00	300,76
372,3	283,62	221,96	120,8	301,00	290,56
409,0	269,46	166,11	104,5	298,00	281,01
451,0	248,47	118,00	82,7	292,00	263,91
457,4	244,81	111,85	56,5	280,00	237,57
		Propane			
225	370,00	370,00	150,00	357,18	359,22
300	367,18	359,22	104,00	359,61	329,37
347	359,61	328,43	80,40	351,23	303,40
381	351,23	287,80	62,20	341,71	277,47
409	341,71	240,10	47,10	330,70	251,65
434	330,70	184,97	33,90	317,42	225,66
		Pentane			
400	448,55	411,49	197	469,95	469,25
344	463,15	450,55	115	460,15	450,02
286	469,25	467,95	100	455,64	446,80
216	470,05	470,01	91	451,95	434,15
		Heptane			
332,3	534,99	500,81	142,0	534,99	511,66
303,8	537,99	524,98	167,3	537,99	529,19
286,7	538,99	533,35	181,8	538,99	535,03
252,6	539,67	539,67	212,2	539,79	539,72
240,9	539,85	539,80	224,2	539,85	539,81

TABLE 2. Comparison of ρ—T Data on Spinodal Curve for n-Hexane

ρ', kg/m³	T'_s, K, [15]	T'_s, K, C_V data of [13]	δ, %, divergence
293,26	504,45	504,36	0,02
310,56	500,15	499,31	0,17
323,42	495,55	494,72	0,17
342,23	488,15	480,56	1,57
352,61	483,15	476,49	1,36
366,70	475,25	469,92	1,13
374,81	470,25	464,21	1,3
381,10	466,15	453,19	2,8

curves calculated by the method described above with those obtained by Skripov [15] from PVT measurements in the metastable region. The good agreement between these results indicates the reliability of the method.

NOTATION

$C_V^* = C_V T_c / P_c V_c$, $\varphi = V/V_c$, $\tau = T/T_c$, reduced heat capacity, specific volume, and temperature; T_c, P_c, V_c, critical temperature, pressure, and volume; α, critical index of isochoric heat capacity; A_s, critical amplitude. Subscripts: s, value on spinodal curve; c, on coexistence curve; δ, relative deviation.

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