Nonclassical critical behavior of the square-well fluid. II.
The specific-heat function C_v and its exponent α

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The Yvon-Born-Green (YBG) theory with Kirkwood superposition is used to determine the critical exponent α for a square-well fluid, where $C_v \sim |T - T_c|^{-\alpha}$ and $T > T_c$. The value obtained, $\alpha = 0.30 \pm 0.01$, when taken in conjunction with the exponents γ, β, and δ determined previously by the authors, is found to be consistent with the two inequalities that involve all four exponents. Finally, as was reported earlier by investigators using the Percus-Yevick theory, extrema in C_v are found in the stable fluid region using the YBG theory.

In recent years, the authors have been involved in a study of the critical exponents for the Yvon-Born-Green (YBG) equation with the Kirkwood superposition approximation for a system of square-well molecules.[1,2] In this paper we report a calculation for the critical exponent α and show evidence of specific heat extrema for this same system.

The critical exponent α is defined along the critical isochore by

$$C_v \sim |T - T_c|^{-\alpha},$$

where the expression for C_v is obtained by differentiating the energy equation of state. The reduced specific heat for a square-well system C_v^* is expressed as

$$C_v^* = \frac{3}{2} + \frac{\lambda_0}{2}\theta^2 \frac{\partial}{\partial\theta}\left[\int_1^R r^2 g^{(2)}(r)dr\right], \quad (1)$$

where $R = \sigma_2/\sigma_1$, λ_0 is the reduced density ($=4\pi\rho\sigma_1^3$), and θ is the reduced reciprocal temperature ($=\epsilon/kT$). Here, as in Ref. 2, a value of 4.55 ± 0.05 was assigned to the reduced critical density, λ_{0c}, for a system of square-well molecules with $R = 1.85$. The YBG equation with the Kirkwood superposition approximation was solved for the pair correlation function $g^{(2)}(r)$ along the critical isochore using the same numerical techniques and imposing the same criteria for accuracy as reported in Refs. 1 and 2. Using these pair correlation functions, the specific-heat data listed in Table I were determined by performing the differentiation

in Eq. (1) both numerically and graphically. The difference between the two techniques was found to be negligible. The exponent α was then determined from a log-log plot of C_v^* and $(\theta - \theta_c)/\theta\theta_c$, using the data of Table I, where θ_c, the reduced reciprocal critical temperature, was previously determined[2] to be 0.37405 ± 0.00005. A value of $\alpha = 0.30 \pm 0.01$ was obtained, with the error in our
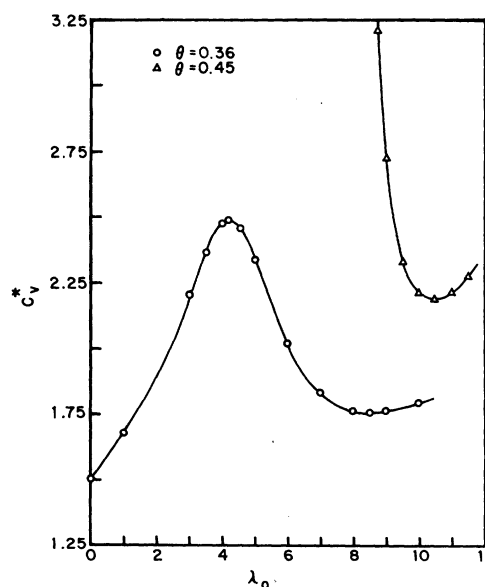

FIG. 1. C_v^* as a function of the reduced density λ_0 for the isotherms $\theta = 0.36$ (supercritical) and $\theta = 0.45$ (subcritical).

TABLE I. C_v^* as a function of θ at $\lambda_{0c} = 4.55$.

θ	C_v^*
0.310	1.756
0.320	1.805
0.330	1.873
0.340	1.974
0.350	2.148
0.360	2.507
0.366	2.963
0.368	3.257
0.369	3.462
0.370	3.721
0.371	4.046
0.3715	4.188

estimate determined by taking into account the uncertainty in the values of C_v^*, λ_{0c}, and θ_c and allowing for error in the graphical techniques used.

In Table II we compare the critical exponents of the YBG theory with those of experiment, the Ising model, and the van der Waals (classical) model. The value of $\alpha = 0.30 \pm 0.01$ reported herein, although higher than one might expect, does not violate the Griffiths inequalities,[7]

$$\gamma(\delta + 1) \geq (2 - \alpha)(\delta - 1)$$

and

$$\beta(\delta + 1) \geq 2 - \alpha$$

when used in conjunction with the three exponents (γ, β, δ) determined previously by the authors.[1,2] However, given the uncertainties of the YBG square-well exponents stated in Table II, one finds that only the second of the above two inequalities could be an equality. A reason for this inconsistency is now proposed. We note that α was

computed using the statistical-mechanical energy equation, while γ, β, and δ were all obtained using statistical-mechanical compressibility equation computations.[1,2] In a rigorous statistical-mechanical theory, the thermodynamics resulting from the energy equation and from the compressibility equation are equivalent. However, for an approximate theory, such as the YBG theory with superposition approximation, the energy and compressibility descriptions of the thermodynamics may be different; the possible discrepancy is related to the neglect of all except the 1,2-irreducible diagrams in the graph theoretical representation of the Kirkwood closure.[8] From a structural point of view, the main difference between the energy equation and the compressibility equation is that the energy equation uses short-range $g^{(2)}(r)$ information, while the compressibility equation is strongly dependent on long-range $g^{(2)}(r)$ behavior.[9] To generate an α using methods consistent with our determination of the other three exponents γ, β, and δ, one would have to employ the compressibility equation of state in concert with the thermodynamic relationship

$$T \left[\frac{\partial^2 P}{\partial T^2} \right]_V = \left[\frac{\partial C_v}{\partial V} \right]_T ,$$

where V is volume, an undertaking which requires considerably more computational effort to determine α than was employed in this paper. One might expect that such a computation would produce an α more consistent with scaling. However, it is noteworthy that the use of only short-range $g^{(2)}(r)$ information, as in the energy equation, does produce a nonclassical value of α. Alder, Young, and Mark[10] used molecular dynamics (up to 500 particles) to study a square-well fluid; despite sampling only short-range correlations (which pro-

TABLE II. Comparison of the critical exponents for the YBG theory, the Ising model, and the van der Waals (classical) model with experiment.

	Experiment (Refs. 3, 4, and 5)	van der Waals (Ref. 6)	Ising (Ref. 4)	YBG (Refs. 1 and 2)
γ	1.25 $\pm$0.03	1	1.250$\pm$0.003[a] 1.241$\pm$0.002[b]	1.23 $\pm$0.02
β	0.325$\pm$0.004	0.5	0.312$\pm$0.002[a] 0.325$\pm$0.002[b]	0.330$\pm$0.008
δ	4.5	3	4.8	4.4 $\pm$0.2
α	0.2 $\pm$0.2	0	0.125$\pm$0.020[a] 0.110$\pm$0.005[b]	0.30$\pm$0.01

[a]Estimates from high-temperature series.
[b]Estimates from renormalization-group methods.

duced *classical* values of γ, β, and δ), they determined α to have the nonclassical value of 0.2 ± 0.1 in their study. This suggests that the exponent α may be insensitive to the representation used for its calculation.

The singularity in the specific heat at the critical point has associated with it extrema in C_v in the stable fluid regime. For isotherms just above the critical isotherm, C_v exhibits both a maximum and a minimum. However, for isotherms below the critical temperature, only a minimum C_v value is found, on the liquid side of the coexistence region. This phenomenon is seen in experiment and is also reported in the work of Bearman, Theeuwes, Bearman, Mandel, and Throop[11] on the Percus-Yevick (PY) equation using a Lennard-Jones 12-6 potential. In order to determine if the YBG equation with the Kirkwood superposition approximation for square-well molecules also displays this specific-heat extrema behavior, a study of two isotherms, $\theta = 0.360$ (supercritical) and $\theta = 0.450$ (subcritical) was carried out. A plot of C_v^* versus λ_0 for these two isotherms is presented in Fig. 1. As can be seen from the figure, the supercritical isotherm, $\theta = 0.360$, displays a maximum value for

C_v^* at $\lambda_0 \cong 4.2$ and a minimum value at $\lambda_0 \cong 8.5$, while the subcritical isotherm, $\theta = 0.450$, shows only a minimum value at $\lambda_0 \cong 10.5$. These minima and maximum are in very good agreement both with experiment and the work of Bearman, Theeuwes, Bearman, Mandel, and Throop[11] on the PY equation, previously cited. As both the YBG and PY theories produce quite similar extrema in C_v, and the YBG theory exhibits nonclassical critical behavior, one might expect the PY theory to be nonclassical as well. However, Rowlinson[12] has carried out a study of the critical-point behavior of the PY theory, and has found that the PY theory yields classical critical exponents only (as does the hypernetted chain theory).

ACKNOWLEDGMENTS

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