

With the correct kernel, Eq. (33) of Lakatos becomes

$$\partial^2 g(\theta) / \partial \theta^2 = -g(\theta) - 4c(a^2 + b^2)f(\theta)g(\theta) - 16abc f(\theta + \frac{1}{2}\pi)g(\theta + \frac{1}{2}\pi), \quad (3)$$

where the last term is missing in Lakatos' expression. With this term the proof is not applicable.

Based on a somewhat different observation, Straley arrived at a conclusion similar to ours at the same time.² We have solved the integral equation numerically. The solution indeed showed a phase transition. This transition from an isotropic phase to a nematic phases

is accompanied by another from a nematic to a smectic phase due to a translational model. In our estimation, this transition seems to take place at $v = V/N = 1.4ab$ after the molecules are lined up. This value 1.4 is very close to what Alder and Wainwright obtained for hard-disk particles.³ In fact, the physical mechanism for this transition is the same as the case of disks.

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¹ K. Lakatos, *J. Chem. Phys.* **50**, 3822 (1969).

² J. P. Straley (private communication).

³ B. J. Alder and T. E. Wainwright, *Phys. Rev.* **127**, 359 (1962).

Reply to Phase Transitions in Two-Dimensional Liquid Crystals

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In the preceding Comment Ishihara and Wadati state that they have found a phase transition in a two-dimensional gas of long thin rods, contrary to results I presented in a previous paper.¹ However, the model I considered was one of rods with *no width* as specifically stated preceding my Eq. (20), while Ishihara and Wadati's calculation corresponds to a finite width.

Straley² arrived at the conclusion that there is a phase transition even in a system with my kernel by observing that I did not have a sufficient number of boundary conditions to uniquely solve the problem. I agree with this assertion.

¹ K. Lakatos, *J. Chem. Phys.* **50**, 3822 (1969).

² J. P. Straley, *Phys. Rev. A* **4**, 675 (1971).

Negative Third Virial Coefficients of Methanol

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Recently, Kell and McLaurin¹ reported new values of the second and third virial coefficients of methanol over the temperature range 150–300°C. Their reported third virial coefficients were negative in the range 150–225°C. Kell and McLaurin interpreted their results in terms of a quasichemical model and the formation of dimers and trimers. The purpose of this note is to indicate that Kell and McLaurin's results for the third

virial coefficient can also be interpreted in terms of an intermolecular potential model which includes multipolar interactions up to the quadrupole–quadrupole interaction and a Lennard-Jones (12–6) central term.

Monchick and Mason² determined Stockmayer potential parameters for methanol from its gaseous viscosity data. If we assume that these parameters would not be changed very much by the inclusion of quadru-

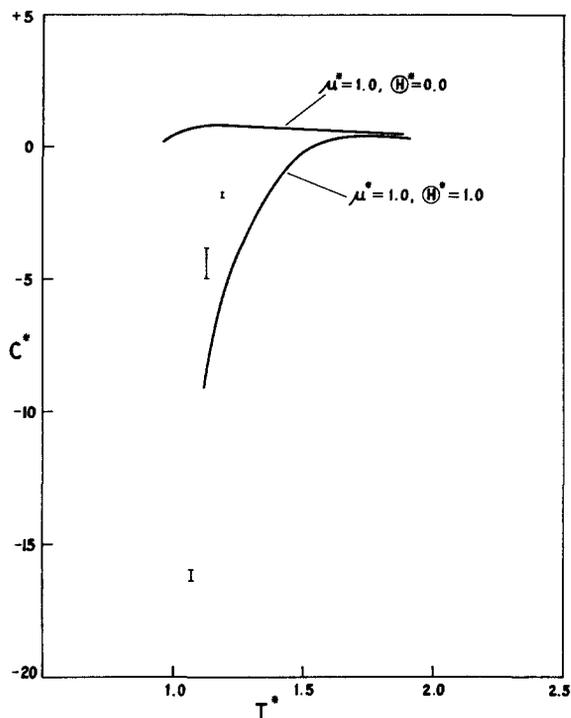


FIG. 1. Reduced third virial coefficients for methanol. The vertical bars indicate the range of Kell and McLaurin's experimental values.

pole moment terms in the collision integral calculation, we can use them in conjunction with quadrupole moment terms in the calculation of third virial coefficients. Johnson and Spurling³ have calculated pairwise additive third virial coefficients for a limited number of parameter sets of a multipolar potential function. In terms of this notation Monchick and Mason's parameters are

$$\epsilon/k = 417K, \quad \sigma = 3.67 \text{ \AA}, \quad \mu^* = 1.0, \quad \Theta^* = 0.0,$$

and from the Fig. 1, it can be seen that these parameters predict positive third virial coefficients over the experimental temperature range. However, the parameter set, $\epsilon/k = 417K$, $\sigma = 3.69 \text{ \AA}$, $\mu^* = 1.0$, $\Theta^* = 1.0$ predicts third virial coefficients which are not very different from the experimental values. The inclusion of other orientation dependent terms in the potential function and the inclusion of nonadditive dispersion forces, together with a smaller value of the quadrupole moment may well improve the agreement.

¹ G. S. Kell and G. E. McLaurin, *J. Chem. Phys.* **51**, 4345 (1969).

² L. Monchick and E. A. Mason, *J. Chem. Phys.* **35**, 1676 (1961).

³ C. H. J. Johnson and T. H. Spurling, *Australian J. Chem.* **24**, 1567 (1971).

Specific Heats of α -Silver Iodide

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Fletcher and co-workers published a series of papers concerning AgI.¹ Their results seem hardly compatible with other observations. Mentioning a few facts about this substance might contribute to an understanding of these rather strange results and interpretations.

Silver iodide occurs in nature in hexagonal crystals, exhibiting a negative thermal volume expansion, and having different signs of linear expansion coefficients in the a and c directions. At about 147°C it transforms into a cubic α phase under marked contraction.

Tubandt, in extremely careful measurements since about 1912 with samples of unusually high purity, gave 144.6°C as the transition temperature. The present author reproduced this value with Tubandt's equipment and all his precautions. The method consisted in having highest purity AgI (cf. Tubandt²) molten and subsequently solidified in appropriate porcelain U tubes, and conductivity measured as a function of temperature. In our measurements of specific heats, started ca. 1952, and continuously

improved, we were not able to reproduce this temperature. The most probable explanation seems to be as follows: after cooling to the transition point and with beginning transformation the volume of the solid inside the tube tends to increase, keeping the inside under high pressure and delaying transformation, enhanced by the contraction of the porcelain. At a certain pressure the tube breaks (in 100% of all experiments) and transformation is completed.

The wholly ionic conductivity of AgI starts with $1.31 \Omega^{-1} \text{ cm}^{-1}$ at the transformation (144.6°C under Tubandt's conditions) and reaches $2.62 \Omega^{-1} \text{ cm}^{-1}$ at the melting point (555°C). Plotted as a logarithm versus $1/T$ it fits a straight line very well (cf. also Biermann and Jost³), without any singularities. The conductivity is, by a factor of 2 to 4, higher than that of best conducting sulfuric acid at (European) room temperature (18°C).

The structure of α -AgI is roughly described as a body-centered iodide ion lattice, with silver ions dis-