

## ONE-DIMENSIONAL MODEL WITH A FLUID-SOLID-TYPE PHASE TRANSITION\*

BY A. FULIŃSKI

Department of Theoretical Physics, Institute of Physics, Jagellonian University, Cracow\*\*

(Received December 28, 1977)

Condensation in one-dimensional system of hard rods is discussed. Each of  $N$  particles interacts with  $N_0 < N$  neighbours by a linear attractive potential of the strength  $B$ . The thermodynamical limit  $N \rightarrow \infty$  is performed simultaneously with the Van der Waals limit such that  $B \rightarrow 0$  with  $BN^2 = \text{finite}$ , and  $N_0 \rightarrow \infty$  with  $\xi = N_0/N = \text{finite}$ . When the fraction  $\xi$  of particles being within the interaction range of a given particle is considered as a variational parameter minimizing the Gibbs free energy, the phase transition of first order appears. The phase transition persists up to  $T \rightarrow \infty$  (i. e., has no critical temperature), resembling in this respect the fluid-solid phase transition. This is in contrast with the conventional Kac-Uhlenbeck-Hemmer theory, in which the thermodynamic limit precedes the Van der Waals one, and which predicts the first order phase transition of the gas-liquid type with the finite critical temperature.

### 1. Introduction

One-dimensional systems of particles with finite-range interactions have no phase transitions [1]. Kac, Uhlenbeck, and Hemmer (KUH) showed [2] that the situation is different when the potential has an infinite range. They considered a one-dimensional system of  $N$  hard rods, confined in a length  $L$ , and interacting with each other through a potential with long-range attractive part of the form

$$V_{\text{att}}(r) = -\alpha\gamma e^{-\gamma r}. \quad (1)$$

The problem of the calculation of partition function was set in the form of an integral equation and it was showed that the free energy and the equation of state of the considered system are connected with the greatest eigenvalue of this equation. The eigenvalues are functions of the temperature  $T$  and pressure  $p$  of the system, and the greatest one is to be determined variationally (cf. especially Baxter's version [3] of the KUH theory, and the paper by Ishihara and Wadati [4]). Now, if first the thermodynamic ( $N \rightarrow \infty$ ,  $L \rightarrow \infty$ ,

\* This work was partly supported through Project No W. 04.3.17.

\*\* Address: Instytut Fizyki UJ, Reymonta 4, 30-059 Kraków, Poland.

$N/L = \text{finite}$ ) limit is taken for finite interaction range ( $\gamma \neq 0$ ), and after this limit the Van der Waals limit  $\gamma \rightarrow 0$  (i. e., interaction range  $\rightarrow \infty$ ) is performed, one may show the existence of a phase transition of first order with finite critical temperature, resembling thus the gas-liquid phase transition. KUH conclude that, for the phase transition to appear, it is necessary to take the limits in the required order (the KUH condition). Indeed, if the required succession is reversed, or if both limits are taken simultaneously, all contributions from  $V_{\text{att}}$  vanish identically and thus there is no phase transition<sup>1</sup>.

The KUH theory, its consequences, generalizations, and specializations, have been widely discussed (cf., e. g., [3–12]). In general, there is an agreement concerning the necessity of the KUH condition for the appearance of the phase transition. In this paper we want to present a counterexample: we are going to show that the system of hard rods with linear (“gravitational”) interactions of limited range, discussed by Isihara and Wadati [4] from the point of view of the KUH theory, exhibits a first-order phase transition also when the thermodynamic and Van der Waals limits are taken simultaneously with  $\gamma L = \text{finite}$ . This phase transition, however, persists up to  $T = \infty$ , i. e., does not possess the critical temperature. On the other hand, it vanishes at the ground state,  $T = 0$ . In this case the phase transition is thus rather of the fluid-solid, than gas-liquid, type. We infer thus that the phase transition is introduced into the theory rather through the variational procedure than by the definite sequence of the limiting procedures, although the latter influences the character of the resulting transition.

## 2. $N$ -particle partition function

Consider the same system as Isihara and Wadati (IW) [4], that is, a one-dimensional system of  $N$  hard rods of length  $\sigma$ , confined in a box of length  $L$ , and interacting with each other through a linear potential of the form:

$$V(r) = \begin{cases} \infty & r < \sigma, \\ -A + Br, & r > \sigma. \end{cases} \quad (2)$$

Assume, after IW, that the interaction (2) has — for a finite system — a finite range, expressed by means of the number  $N_0 < N$  of other particles interacting through the potential (2) with a given particle. The total potential energy is thus:

$$\phi(r^N) = \sum_{i=1}^{N-1} \sum_{j=i+1}^{M_i} V(r_{ij}), \quad M_i = \min(N, N_0 + i), \quad (3)$$

i. e.,

$$\phi(r^N) = \phi_0(r^N) - \frac{1}{2} AN_0(2N - N_0 - 1) + B \sum_{j=1}^N v_j r_j, \quad (4)$$

$$v_j = (j - N + N_0)\theta(j - N + N_0) - (N_0 + 1 - j)\theta(N_0 + 1 - j), \quad (4a)$$

<sup>1</sup> The KUH condition can be weakened [5]: both limits can be performed simultaneously, if the length of the interaction range is kept negligible comparing with the length of the system, i. e., if  $\gamma L \rightarrow 0$  for  $L \rightarrow \infty$ ,  $\gamma \rightarrow 0$ .

where  $\theta(x)$  is the step-function, and  $\phi_0(r^N)$  represents the repulsive part of the potential. Note that, in contrary to the IW formulation, the above notation does not exclude  $N_0 \geq \frac{1}{2}N$ . The  $N$ -particle pressure partition function is (the hard interactions with walls at  $r = 0$  and  $r = L$  are included):

$$Z_N(p, T) = \lambda^{-N} \alpha \int_0^\infty dL e^{-\alpha L} \theta(L - N\sigma) \int_0^L dr^N e^{-\beta \phi(r^N)}, \quad (5)$$

with  $\alpha = \beta p$ ,  $\beta = 1/kT$ ,  $\lambda = (h^2/2\pi mkT)^{1/2}$ , and other symbols have their usual meaning. Taking into account Eqs. (2) and (4) we get, with the help of the substitution  $r_j - j\sigma = x_j$ ,

$$Z_N(p, T) = \lambda^{-N} \alpha e^{-\alpha N\sigma + \beta \kappa} \int_0^\infty dx e^{-\alpha x} \int_0^x dx_N \int_0^{x_N} dx_{N-1} \dots \int_0^{x_2} dx_1 \exp(-\beta B \sum_{j=1}^N v_j x_j), \quad (6)$$

where

$$\begin{aligned} \kappa &= \frac{1}{2} AN_0(2N - N_0 + 1) - B \sum_{j=1}^N j v_j \sigma \\ &= \frac{1}{2} AN_0(2N - N_0 + 1) - \frac{1}{6} B\sigma(N_0 + 1)(3N - 2N_0 - 1)N_0. \end{aligned} \quad (6a)$$

The multiple integral in Eq. (6) may be evaluated directly:

$$\begin{aligned} Z_N(p, T) &= (\lambda e^{\alpha\sigma})^{-N} e^{-\beta \kappa} \alpha \int_0^\infty dx e^{-\alpha x} \int_0^x dx_N e^{\gamma_N(x - x_N)} \\ &\int_0^{x_N} dx_{N-1} e^{\gamma_{N-1}(x_N - x_{N-1})} \dots \int_0^{x_2} dx_1 e^{\gamma_1(x_2 - x_1)} = (\lambda e^{\alpha\sigma})^{-N} e^{\beta \kappa} \prod_{j=1}^N (\alpha - \gamma_j)^{-1}, \end{aligned} \quad (7)$$

with

$$\begin{aligned} \gamma_j &= \beta B \sum_{i=1}^j v_i = \frac{1}{2} \beta B \{ (j - N + N_0)(j - N + N_0 + 1) \theta(j - N + N_0) \\ &\quad - N_0(N_0 + 1) \theta(j - N_0) - j(2N_0 - j + 1) \theta(N_0 - j) \}. \end{aligned} \quad (7a)$$

### 3. Thermodynamical limit

Consider now the thermodynamical limit, and assume that the range parameter  $N_0$  goes to infinity together with the total number of particles:

$$N \rightarrow \infty, \quad L \rightarrow \infty, \quad N/L = \text{finite}, \quad (8a)$$

$$N_0 \rightarrow \infty, \quad N_0/N = \xi = \text{finite}. \quad (8b)$$

In order to guarantee the existence of the system we must also have:

$$A \rightarrow 0, \quad B \rightarrow 0, \quad AN = a = \text{finite}, \quad BN^2 = b = \text{finite}. \quad (8c)$$

In this case,

$$\kappa = N\bar{\kappa}(a, b, \xi), \quad \gamma_j = \gamma(b, \xi; j/N).$$

Also,

$$\lim_{N \rightarrow \infty} \frac{1}{N} \sum_{j=0}^N f(j/N) = \int_0^1 dz f(z).$$

The Gibbs free energy per particle is thus:

$$\begin{aligned} g(p, T; \xi) &= - \lim_{N \rightarrow \infty} \frac{1}{N} kT \ln Z_N(p, T; N_0) \\ &= p\sigma + kT \ln(\lambda/\sigma) - a\xi(1-\xi/2) + \frac{1}{2} b\sigma\xi^2(1-2\xi/3) + g_1, \end{aligned} \quad (9)$$

with

$$\begin{aligned} g_1/kT &= \lim_{N \rightarrow \infty} \frac{1}{N} \sum_{j=1}^N \ln [\alpha\sigma - \gamma(j/N)\sigma] \\ &= \int_0^1 dz \ln \left\{ \alpha\sigma - \frac{1}{2} \beta\sigma b [(z-1+\xi)^2 \theta(z-1+\xi) - \xi^2 \theta(z-\xi) - z(2\xi-z)\theta(\xi-z)] \right\} \\ &= \ln(\sigma b/2kT) + 2\xi \ln P + 2R \ln \frac{R+\xi}{R-\xi} + (1-2\xi) \ln(P+\xi^2) - 4\xi \\ &\quad + \theta(\xi - \frac{1}{2}) \left\{ 2R \ln \frac{R+1-2\xi}{R-1+2\xi} + Q \ln \frac{Q+2\xi-1}{Q-2\xi+1} + 2(2\xi-1) \right. \\ &\quad \left. - (2\xi-1) \ln \left[ 1 - \frac{(2\xi-1)^2}{P+\xi^2} \right] \right\}, \end{aligned} \quad (10)$$

and

$$P = 2p/b, \quad R = (P+\xi^2)^{1/2}, \quad Q = [2P+1-2(1-\xi)^2]^{1/2}. \quad (10a)$$

The limit  $\xi \rightarrow 0$ , such that  $a\xi = AN_0 = \text{finite}$ ,  $b\xi^2 = N_0^2 B = \text{finite}$ ,  $A, B = \text{finite}$ , of the formula (9), is the IW result:

$$\frac{G}{kT} = \ln(\lambda/\sigma) + Z - 2tx + x^2 - \ln(Z+x^2), \quad (11)$$

with

$$Z = p\sigma/kT, \quad t = A/\sqrt{2\sigma BkT}, \quad x = N_0\sqrt{B\sigma/2kT}. \quad (11a)$$

#### 4. The equation of state

The inspection of the Gibbs free energy  $g$ , considered as the function of the range parameter  $\xi$ , shows that  $g(\xi)$  has a minimum at some value of  $\xi = \xi_0 < \frac{1}{2}$ . For  $\xi > \frac{1}{2}$ ,  $g(\xi)$  attains its lowest value at  $\xi = 1$ , although at this point  $(\partial g/\partial \xi) \neq 0$ .  $\xi_0$ ,  $g(\xi_0)$ , and  $g(\xi = 1)$  depend on the pressure  $P$  (at a given temperature  $T$ ). For sufficiently low pressures,

$g(\xi_0)$  is the lowest value of all the values of  $g(\xi)$  over the whole physical range  $0 \leq \xi \leq 1$ . However, when the pressure is raised,  $g(\xi_0)$  increases stronger than  $g(\xi = 1)$ , and above some pressure  $P = P^*$ , it is  $g(\xi = 1)$  which is now the lowest value of  $g(\xi)$  over the whole range of  $\xi$ :

$$\inf_{\xi} g(\xi) = \begin{cases} g(\xi = \xi_0), & \xi_0 < \frac{1}{2}, & \text{for } P < P^*, \\ g(\xi = 1) & & \text{for } P > P^*. \end{cases} \quad (12)$$

This behaviour is shown in Fig. 1a, where the quantity

$$\frac{\Delta g}{kT} = \frac{1}{kT} [g(\xi) - g(\xi = 1)]$$

is drawn vs.  $\xi$  for a few values of  $P$ , for  $(2kT/b\sigma) = 0.1$ ,  $(a/b\sigma) = 0.2$ .

The parameter  $\xi$  is the fraction of particles within the range of interaction with the chosen particle. Assume, after IW, that  $\xi$  is the variational parameter, i. e., that the considered model is interpreted in such a way that the actual value of  $\xi$  is to be determined by the lowest possible value of the Gibbs free energy, corresponding to the physically compatible values of  $\xi$ . The interpretation of the variational treatment of the number  $N_0$  of

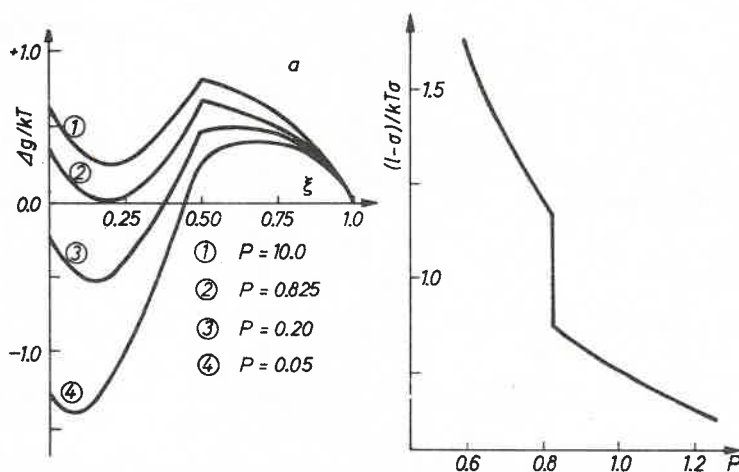


Fig. 1. Evidence of the phase transition at finite temperature;  $2kT/b\sigma = 0.1$ ,  $a/b\sigma = 0.2$ . (a) Dependence of the Gibbs free energy on the range parameter  $\xi$ , for some values of the pressure  $P = 2p/b$ . (b) Equation of state: dependence of the specific volume  $l$  vs pressure  $P$ , corresponding to the least values of  $g(\xi)$ . For convenience, quantities  $\Delta g/kT$  and  $(l-\sigma)/\sigma kT$ , instead of  $g$  and  $l$ , are shown

particles contained within the range of attraction of one particle, was given by IW. The only difference between our present case and the model considered by IW is that IW keep — according to the KUH ideas — the interaction range  $N_0$  and the interaction strength  $B$  constant and finite during the thermodynamic limit  $N \rightarrow \infty$ , and perform the limit  $N_0 \rightarrow \infty$  at the end (hence  $\xi = N_0/N \rightarrow 0$ ), whereas here  $N_0 \rightarrow \infty$  together with  $N$  so that  $\xi = \text{finite}$ .

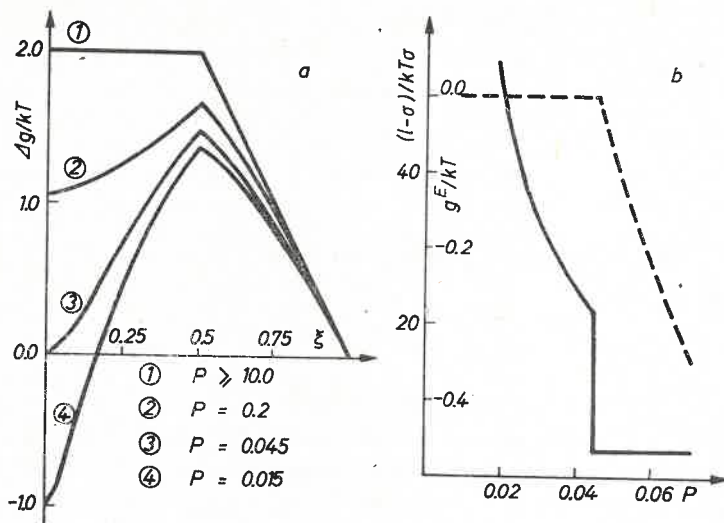


Fig. 2. The same as in Fig. 1, in the limit  $T \rightarrow \infty$ . Dashed line in Fig. 2b shows additionally the pressure dependence of the excess Gibbs free energy  $g^E = g - g_{id}$ , corresponding to  $\inf g(\xi)$

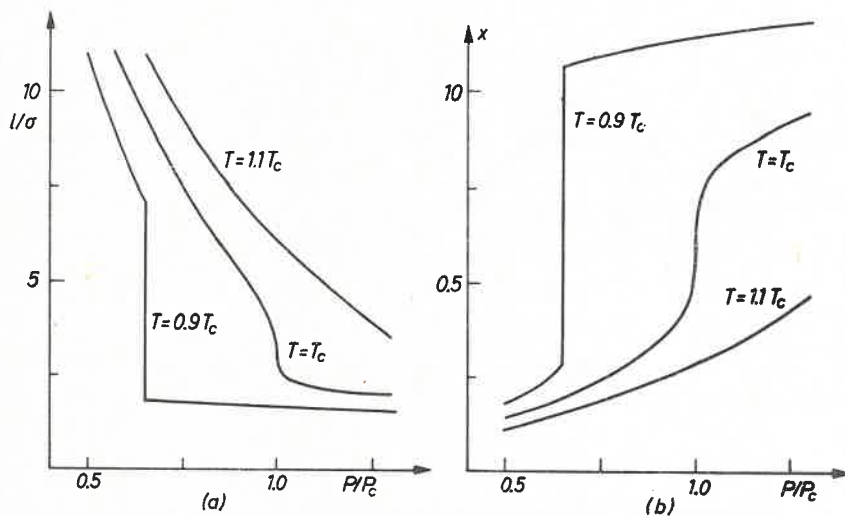


Fig. 3. Illustration of the IW model calculated according to the KUH prescription. (a) Three isotherms obtained from Eq. (11). The curve labelled  $T = T_c$  is the critical isotherm.  $T_c = 4A^2/27Bk\sigma$ ,  $P_c = kT_c/8\sigma$ . (b) Values of the range parameter  $x$ , corresponding to the thermodynamic states from (a)

With the variational interpretation, Eq. (12) describes the phase transition at  $P = P^*$ . This is shown in Fig. 1b, where  $(l-\sigma)/\sigma kT$ , corresponding to  $\inf g(\xi)$  from Fig. 1a, is drawn as the function of pressure,  $l = (\partial g/\partial P)_T$  being the specific volume (length per particle) of the system. In the high-density (condensed) phase  $\xi = 1$ , i. e., all particles are within the range of mutual interaction, whereas in the low-density (gas) phase only about 20% of all particles do interact with the chosen one.

The behaviour of the considered model, described above, resembles so far that of the IW model, and in general, the results of the general KUH theory. However, the phase transition obtained in the latter theories possesses the critical temperature, whereas in the present model the phase transition persists at arbitrarily high temperatures. This is illustrated in Fig. 2, where the limit  $T \rightarrow \infty$  of the Fig. 1 is shown, and in Fig. 3, where the equation of state resulting from the IW formula, Eq. (11), is presented. On the other hand, the phase transition vanishes at  $T = 0$ : it is easy to see from Eq. (9) that in the ground state the system is always (i. e., at every pressure) in one phase, with minimal value of the Gibbs free energy obtained at  $\xi = \min(a/b\sigma, 1)$ . Hence, when the sequence of limits fulfilling the KUH condition leads to the phase transition possessing the critical point, i. e., resembling the gas-liquid transition, the simultaneous increase of both the size of the system and of the interaction range results also in the appearance of the phase transition, but rather of the fluid-solid type without critical temperature.

## REFERENCES

- [1] L. Van Hove, *Physica* **16**, 137 (1950).
- [2] M. Kac, G. E. Uhlenbeck, P. C. Hemmer, *J. Math. Phys.* **4**, 216 (1963).
- [3] J. Baxter, *Phys. Fluids* **8**, 687 (1965).
- [4] A. Isihara, M. Wadati, *Progr. Theor. Phys.* **48**, 1493 (1972).
- [5] P. C. Hemmer, J. L. Lebowitz, in *Phase Transitions and Critical Phenomena*, Edited by C. Domb and M. S. Green, Vol. 5b, Acad. Press, London-New York 1976.
- [6] R. M. May, *Phys. Lett.* **12**, 15 (1964).
- [7] J. L. Lebowitz, O. Penrose, *J. Math. Phys.* **7**, 98 (1966).
- [8] J. B. Jalickee, H. J. F. Siegert, D. J. Vezetti, *J. Math. Phys.* **10**, 1442 (1969).
- [9] N. G. Van Kampen, *Physica* **48**, 313 (1970).
- [10] P. C. Hemmer, G. Stell, *Phys. Rev. Lett.* **24**, 1284 (1970).
- [11] J. B. Jalickee, F. W. Wiegel, D. J. Vezetti, *Phys. Fluids* **14**, 1041 (1971).
- [12] G. Stell, P. C. Hemmer, *J. Chem. Phys.* **56**, 4274 (1972).