

Anomalous phase behavior of quasi-one-dimensional attractive hard rods

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Abstract

We study a two-state model of attractive hard rods using the transfer matrix method, where the centres of the particles are confined to a straight line, but the orientations of the rods can be parallel or perpendicular to the confining line. The rods are modelled as hard rectangles with length L and width D and decorated with attractive sites at both ends of the rectangles. We find that the particles align parallel to the line and form long chains at low densities, while they turn out of the line and forms a Tonks gas at high densities. With increasing the stickiness between the rods, the structural change between parallel and perpendicular states becomes stronger and the pressure vs. density curve becomes almost a horizontal line at the transition pressure. We show that such a behaviour is reminiscent of the first-order phase transition. This manifests in the validity of lever-rule of the phase transitions for very sticky cases.

1. Introduction

The rod-like particles exhibit special ordering behaviour in confining geometries, which makes them the potential applicants for nanodevices and nanosensors [1]. Such particles are the carbon nanotubes and the gold nanowires with special electronic and optical properties. A big issue in the practical use of these particles is to increase the surface coverage, create large monodomains and enhance the orientation order on flat surfaces [2-5]. To give theoretical guidance in this direction, it is important to understand the ordering behaviour of rod-like particles in several confining geometries such as circle, square, stripe and line [6-14].

A special class of the confined systems is the one-dimensional (1D) fluid, where the centres of the particles are forced to move on a straight line. The thermodynamic and structural properties have been determined exactly for several 1D fluids [15-18], where short range attractions are added to the hard core interactions. The common feature of these 1D systems is the lack of thermodynamic singularity, which exclude the possibility of first order phase transitions [19]. However, the absence of phase transition can be proved rigorously only for a class of 1D fluids, which is based on the Perron-Frobenius-Jentzsch theorem [20]. The well-known exception is the 1D van der Waals fluid, where the attraction's range (strength) goes to infinity (zero). In this system a first order vapour-liquid phase transition emerges, which can be described with the famous van der Waals equation of state [21, 22]. It is more difficult to predict the phase behaviour of the system if some out-of-line orientational and positional freedom added to the 1D system, which is usually called as quasi-one-dimensional (q1D) system. The out-of-line orientational freedom gives rise to structural change in the orientational ordering in the system of hard non-spherical particles [23-25]. If the particles are placed on 1D lattice and allowed to overlap with some cost, first order phase transitions can occur easily [26]. It has been shown recently in [27] that the free energy has an infinite number of singularities as a function of density in the q1d system of soft needles. Kantor and Kardar reported the jamming behaviour

of the q1d system of non-spherical particles in the vicinity of close packing density, where the particles are free to rotate in a plane [28, 29]. In addition to these, the kinetic of the domain walls and the glassy behaviour of q1D systems with rotational freedom are studied [30, 31]. In the system of freely rotating associating particles, which is related to our work, it is beneficial to use 1D spatial confinement to enhance the association and induce orientational order within the clusters [32-35]. The out-of-line positional freedom complicates further the phase behaviour of the particles, because very complicate tilted and even chiral close packing structures emerge, which depends on both the shape and the extent of the out-of-line freedom [36-38]. For example, the hard disks form a zig-zag close packing structure in very narrow q1D channels, where only first neighbour interactions are allowed [39-41]. Finally we note that the phase behaviour of q1D systems of hard disks is still a hot topic because of the emerging jamming, glass formation and caging phenomena [42-50]. These results show that our knowledge of the ordering mechanism of q1D systems is far from complete.

In this study we examine the possibility of first order phase transitions in q1D systems, where both the repulsive and attractive interactions are present. For the sake of simplicity, the centres of the particles are fixed to a horizontal line and only the horizontal and vertical orientational states are taken into account. To induce a competition between parallel and perpendicular orientational ordering, the shape of the particle is anisotropic and both ends of the particle are decorated by attractive patches. Such models enable us to examine the competition between the association energy and the entropy, because the association favours the horizontal ordering, while the entropy the vertical one. The energy minimum corresponds to a perfect horizontal order, where all particles are in bonds and they form an infinitely long chain. In contrast to this, the close packed structure is vertically ordered, i.e. the entropy must destabilize the horizontal order with increasing density. In general, the entropy tries to maximize the available microstates through the competition of orientational and packing entropy terms. The orientational entropy favours the random orientational order, while the packing one gives rise to orientational and positional ordering. In this regard, the hard rod model is the famous example, which undergoes an isotropic-nematic phase transition with increasing density. In hard rod models, the orientational entropy stabilizes the isotropic phase, while the packing one is responsible for the nematic one [51, 52]. In the present model of hard rectangles with attractive sites, we show that the energy gain is responsible for the horizontal order at low densities, while the packing entropy gain gives rise to vertical order at high densities. The competition between the horizontal and vertical ordering can be enhanced with increasing the stickiness between the particles, which can terminate into a phase transition. Here we show that even a first order phase transition can occur in the presence of extreme conditions even if the system is q1D.

2. The attractive rectangle model and the transfer matrix method

We consider a system of rectangular particles with their centres confined to a straight line (see Fig. 1). The particles are allowed to move freely on the line, but the orientational freedom is restricted to a horizontal (-) and a vertical state (|). In this two-state model both hard body repulsion and square-well attractions are present, i.e. the hard rectangles with length L and width D are not allowed to overlap, but they can attract each other in the horizontal states. Therefore the pair potential (u) is the well-known square-well potential if both particles are oriented along the confining line, i.e.

$$u_{--}(x) = \begin{cases} \infty, & 0 \leq x \leq L \\ -\varepsilon, & L < x \leq L(1 + \delta) \\ 0, & x > L(1 + \delta) \end{cases}, \quad (1)$$

where x is the distance between two particles, ε is the well-depth and δ is the range of attraction. If one or both of the particles are not in horizontal states, the interaction potential is hard repulsive. Therefore the pair potential for other pairs of orientations is given by

$$u_{-|}(x) = u_{|-}(x) = \begin{cases} \infty, & 0 \leq x \leq \frac{L+D}{2} \\ 0, & x > \frac{L+D}{2} \end{cases}, \quad (2)$$

and

$$u_{||}(x) = \begin{cases} \infty, & 0 \leq x \leq D \\ 0, & x > D \end{cases}. \quad (3)$$

At this point it is worth introducing the stickiness parameter (τ), which connects the Baxter's adhesive or sticky hard body fluids with the square-well one [53-55]. In the case of 1D square-well pair potential, this can be written as

$$\tau := 1/[(\exp(\beta\varepsilon) - 1)\delta]. \quad (4)$$

Note that this equation comes from the equality of the second virial coefficients of 1D square-well and sticky pair potentials. The adhesive limit of square-well potential can be obtained by taking the $\delta \rightarrow 0$ and $\varepsilon \rightarrow \infty$ limits with a condition that the stickiness parameter remains finite. In the following we study square-well and sticky fluids, where only nearest neighbour interactions are present. This condition delimits the range of the attraction into $0 < \delta < 1$. Firstly we study the strictly 1D case, where the orientation of the rectangle is always horizontal. To determine the thermodynamic properties of 1D fluids with short range attractions, the isobaric ensemble proved to be the best [18]. In this ensemble the Gibbs free energy (G) of strictly 1D fluids can be determined from

$$g := \frac{\beta G}{N} = -\ln(K_{--}), \quad (5)$$

where $\beta = \frac{1}{k_B T}$ is the inverse temperature, N is the number of particles, and K_{--} can be obtained from the horizontal-horizontal pair potential ($u_{--}(x)$) as follows

$$K_{--} = \int_0^{\infty} \exp(-\beta u_{--}(x)) \exp(-\beta P x) dx, \quad (6)$$

where P is the horizontal pressure. It will turn out later that this integral is one of the element of a transfer matrix, which is used for the two-state model. From the Gibbs free energy it is easy to derive the equation of state using the standard thermodynamic relationships. From G we can get the inverse of the 1D number density (ρ) as follows

$$\frac{1}{\rho} = \frac{1}{\beta} \frac{dg}{dP}, \quad (7)$$

Inserting Eq. (1) into Eq. (6) and using Eq. (4) we get that

$$K_{--} = \frac{\exp(-\beta PL)}{\beta P} \left(1 + \frac{1 - \exp(-\beta PL \delta)}{\tau \delta} \right). \quad (8)$$

Note that $\beta \varepsilon$ dependence is replaced with τ in Eq. (8). With this trick we can connect the sticky fluid with the square-well one, because the sticky-limit ($\delta \rightarrow 0$ and $\varepsilon \rightarrow \infty$, while τ is constant) simplifies Eq. (8) as follows

$$K_{--} = \frac{\exp(-\beta PL)}{\beta P} \left(1 + \frac{\beta PL}{\tau} \right). \quad (9)$$

Substituting Eq. (8) into Eq. (7) we can obtain the exact equation of state of 1D square-well fluid if $0 < \delta < 1$. Note that van der Waals loop cannot occur in this system as the density always increases with the pressure, i. e. there is no true vapour-liquid phase transition. However, it can be proved that a first order vapour-liquid phase transition occurs in the $\delta \rightarrow \infty$ and $\varepsilon \rightarrow 0$ limits, where all particles interact with all particles [21, 22].

The above formalism can be generalised for particles with orientational degrees of freedom, too, using the transfer matrix method [26]. In our two-state model, we must generalise Eq. (6) as follows

$$K_{ij} = \int_0^{\infty} \exp(-\beta u_{ij}(x)) \exp(-\beta P x) dx, \quad (10)$$

where $i, j = -$ and $|$ describe the horizontal and vertical orientational states, respectively. The K_{--} element is given by Eq. (8), while the cross terms and the out-of-line terms can be obtained from Eq. (10) using Eqs. (2) and (3), respectively. One can easily show that

$$K_{|-} = K_{-|} = \frac{\exp(-\beta P(L+D)/2)}{\beta P}, \quad (11)$$

and

$$K_{||} = \frac{\exp(-\beta PD)}{\beta P}. \quad (12)$$

According to the transfer matrix theory, the largest eigenvalue of the 2x2 K_{ij} transfer matrix is related to the Gibbs free energy, while the corresponding eigenvector can be used to determine the fraction of particles at a given orientation [24-26]. The eigenvalue equation is given by

$$\sum_{i=|,-} K_{ij} \psi_j = \lambda \psi_i, \quad (13)$$

where λ and $(\psi_{-}, \psi_{|})$ are the eigenvalue and eigenvector of the transfer matrix, respectively. The solution of Eq. (13) for the eigenvalue comes from the following determinant

$$\begin{vmatrix} K_{--} - \lambda & K_{-|} \\ K_{|-} & K_{||} - \lambda \end{vmatrix} = 0. \quad (14)$$

As the determinant corresponds to a quadratic equation for the eigenvalue, we get two solutions: λ_1 and λ_2 . The largest eigenvalue, which is given by $\lambda = \max(\lambda_1, \lambda_2)$, is related to the Gibbs free energy density:

$$g = -\ln(\lambda). \quad (15)$$

Using this formula for g , one can determine the equation of state from Eq. (7) as before. The eigenvector of the largest eigenvalue coming from Eq. (13) provides the fraction of particles in “-“ and “|” orientations. Using the normalised solution of Eq. (13) for ψ_{-} and $\psi_{|}$, where the normalisation condition is prescribed by $\psi_{-}^2 + \psi_{|}^2 = 1$, the fractions of the particles in horizontal and vertical directions are given by

$$x_{-} = \psi_{-}^2 \text{ and } x_{|} = \psi_{|}^2. \quad (16)$$

From these mole fractions, it is easy to determine the nematic order parameter, which measures the extent of orientational ordering, since

$$S = x_{-} - x_{|}. \quad (17)$$

We can see that $S=0$ in the isotropic phase, $S=1$ for perfect horizontal, and $S=-1$ for perfect vertical order. Therefore we can distinguish three different structures with this order parameter. Finally we note that we use D to make the pressure and the density dimensionless in the following way: $P^* = \beta PD$ and $\rho^* = \rho D$.

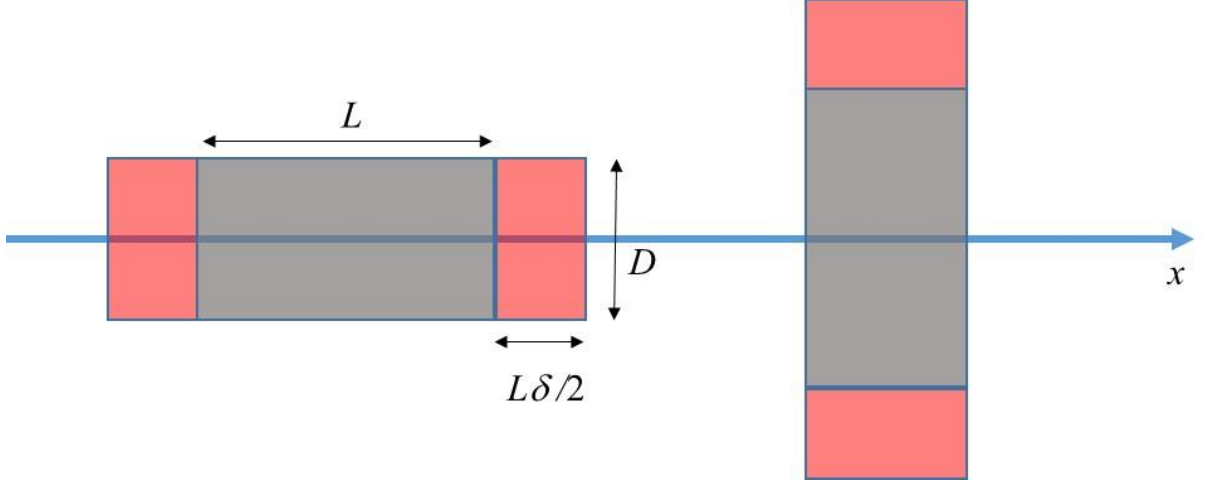


Figure 1. A two-state model of quasi-one-dimensional attractive rods. A hard rectangle with length L and width D is shown in the horizontal (left) and the vertical (right) states. The centre of the particle is restricted to the x axis. The range of the square-well attraction is controlled by δ . The overlap between the grey regions of any two particles is forbidden, while attraction can take place if the pink regions overlap between two particles. The attraction between two neighbouring particles is feasible only if both are parallel to the x axis.

3. Results

In this section, we start with the 1D reference system, where all particles are parallel to the x axis (see Fig. 1) and behave as a 1D square-well fluid. In this case the equation of state is analytical and exact for $\delta < 1$. Using Eqs. (5), (7) and (8) one can find that

$$\frac{1}{\rho^*} = \frac{L}{D} + \frac{1}{P^*} - \frac{1}{\alpha} \frac{\exp(-P^* \delta L/D) L/D}{\tau}, \quad (18)$$

where $\alpha = 1 + (1 - \exp(-P^* \delta L/D)) / (\delta \tau)$. It goes without saying that Eq. (18) becomes identical with the ideal gas law at very low pressures ($P^* = \rho^*$) and ρ^* goes to D/L in the limit of $P^* \rightarrow \infty$, which corresponds to the close packing density of the system. Note that Eq. (18) provides the density as a function of pressure. In the sticky-limit ($\delta \rightarrow 0$) it is even possible to express the pressure as a function of density in the following form

$$P^* = \frac{2\rho^*}{1 - \rho^* L/D + \sqrt{(1 - \rho^* L/D)^2 + 4\rho^* L/D(1 - \rho^* L/D)}/\tau}. \quad (19)$$

In Fig. 2 we show the equation of state for several values of the stickiness parameter (τ) at $L/D=5$. One can see that the maximum value of ρ^* is 0.2, which corresponds to the close packing density. At this value of density the pressure must diverge for any value of τ . It can be shown that Eq. (19) becomes identical with the Tonks's equation of state of hard rods in the $\tau \rightarrow \infty$ limit, where $P^* = \rho^* / (1 - \rho^* L/D)$. We can also see in Fig. 2 that the contribution of the attraction does not result in a loop in the equation of state, i.e. true phase transition cannot occur

in the fluid of sticky hard rods. The effect of attraction is that the pressure can be lowered with decreasing τ , but the shape of the curve does not change. This happens in the fluid of square-well particles (see Eq. 18), too, where only nearest neighbour interactions take place.

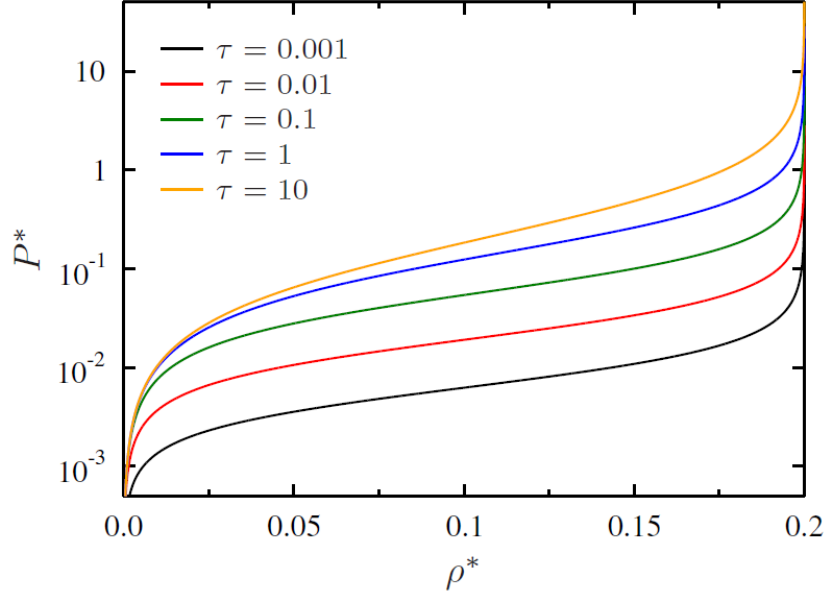


Figure 2. Equation of state of one-dimensional sticky hard rods in pressure ($P^* = \beta PD$) vs. density ($\rho^* = \rho D$) plane. All particles are oriented along the x axis and $L/D=5$. The curves are the results of Eq. (19).

We now continue with the two-state system, where the vertical-horizontal and the vertical-vertical interactions are purely repulsive (see Eqs. (2) and (3)). We can see in Fig. 3 that adding the vertical orientational freedom to the system changes the phase behaviour dramatically. To understand this unusual behaviour, we start with the case of weak attraction ($\tau > 1$), where the hard body interactions are dominant. In the hard body limit, i.e. $\alpha = 1$, the transfer matrix method results in a generalised Tonks equation of state of 1D hard rods, where the packing fraction (η) depends on the pressure. It is easy to show using the transfer matrix method that the equation of state of two-state hard rectangle model is given by

$$\beta P^* = \frac{\rho^*}{1 - \eta}, \quad (20)$$

where $\eta = \rho^* (x_- L/D + x_+)$ is the packing fraction along the line. The fraction of rectangles along the horizontal and vertical directions can be obtained from

$$x_- = \frac{\exp(-P^* L/D)}{\exp(-P^* L/D) + \exp(-P^*)}, \text{ and } x_+ = \frac{\exp(-P^*)}{\exp(-P^* L/D) + \exp(-P^*)}. \quad (21)$$

At very low pressures, Eq. (21) shows that $x_+ = x_-$, i.e. the phase is isotropic in the ideal gas limit. With increasing pressure, it becomes more and more favourable to stay in the vertical

state if $L/D > 1$, because the occupied length of a single particle is $L-D$ distance lower in the vertical state than in the horizontal one. In the close packing limit, when the pressure is extremely high, all particles orient perpendicularly to the confining line as Eq. (21) gives $x_{\parallel} = 1$ and $x_{\perp} = 0$. Regarding the attractive rods, the transfer matrix method does not provide simple equations for the equation of state, x_{\parallel} and x_{\perp} fractions, but they simplify to Eqs. (20) and (21) in the limit of $\tau \rightarrow \infty$. Our results for the equation of state and the order parameter are presented in Fig. 3 for the sticky case ($\delta \rightarrow 0$). We can see that the vertical ordering starts at relatively low pressures ($P^* \sim 1$) for $L/D = 5$ even if the attractive forces are against the vertical order. In this phase, the system behaves like a gas of hard rods with length D , where the pressure is given by $\beta P^* = \rho^* / (1 - \rho^*)$ for any value of τ . Note that we can get this result if $x_{\parallel} = 1$ is inserted into Eq. (20). In the case of $\tau > 1$, the nematic order parameter (S) is decreasing continuously, because the energetic gain is not enough to compensate the packing entropy loss. In contrast to this, the energy plays a crucial role at low and intermediate densities for $\tau < 1$, where the energy gain stabilizes the horizontal order and S saturates at one. Due to the strong attraction, the particles stay parallel to the x axis up to the close packing density of the horizontal phase, where the pressure would diverge without the out of line orientational freedom. This divergence happens at $\rho^* = D/L$. Note that even the equation of state of sticky rods (Eq. (19)) can be applied when $S \approx 1$. We can see that the pressure range of horizontal order and the validity range of Eq. (19) extends with decreasing τ , which is due to the strengthening attraction. Above the horizontal close packing density, the particles must change orientation as the vertical close packing density is always 1. In the case of $L/D = 5$, we can accommodate 5 times more particles in the vertical state than in the horizontal one. Therefore, it is entropically beneficial to undergo a structural change from the horizontal to the vertical phase. We can see in Fig. 3 that the structural change is accompanied with a sudden change of ρ and S with increasing pressure for $\tau < 1$. As τ decreases, this change happens between almost perfect horizontal and vertical phases as S changes from 1 to -1. In addition to this the equation of state becomes very flat and widens with decreasing τ . This reminds us of a first order phase transition, where the coexisting densities are connected with a horizontal tie line at the transition pressure. It is also interesting that the width of the flat region of the equation of state widens with decreasing τ . We found that the flat region extends up to $D/L < \rho^* < 1$ with $\tau \rightarrow 0$, but the pressure of the flat region diverges logarithmically. Therefore the flat region of the equation of state extends to the whole density range for needles ($L/D \rightarrow \infty$) if $\tau \rightarrow 0$. To get a deeper insight into the phase behaviour of the system, it is useful to examine the role of matrix elements of the transfer matrix. We know that the phase behaviour of horizontal order can be described with K_{--} element, while K_{\parallel} accounts for the vertical one. The role of off-diagonal ($K_{-|}$) element is to link the low and high density structures and to produce exact results in the ideal gas limit. If this element is neglected in the matrix, which is called as a level-crossing approximation, we can examine the competition between the horizontal and vertical structures. In this approximation, the eigenvalue of 2×2 diagonal matrix can be obtained from $\lambda = \max(K_{--}, K_{\parallel})$ and the corresponding mole fractions $x_{\perp} = 1$ ($x_{\parallel} = 0$) if K_{--} is higher (lower) than K_{\parallel} . In Fig. 4 we compare the exact results coming from Eqs. (14) and (15) with the results of level crossing approximation for the Gibbs free energy and the

equation of state. We can see that $g = -\ln(K_{\perp})$ and $g = -\ln(K_{\parallel})$ curves cross each other and overestimate slightly the exact Gibbs free energy. With lowering pressure $g = -\ln(K_{\perp})$ merges with the exact g , while $g = -\ln(K_{\parallel})$ does the same with increasing pressure. The poorest agreement occurs, where the two curves cross each other. This cross point corresponds to a first order phase transition on the level of approximation, because the pressures and the chemical potentials of the horizontal and vertical structures are the same. From $K_{\perp} = K_{\parallel}$

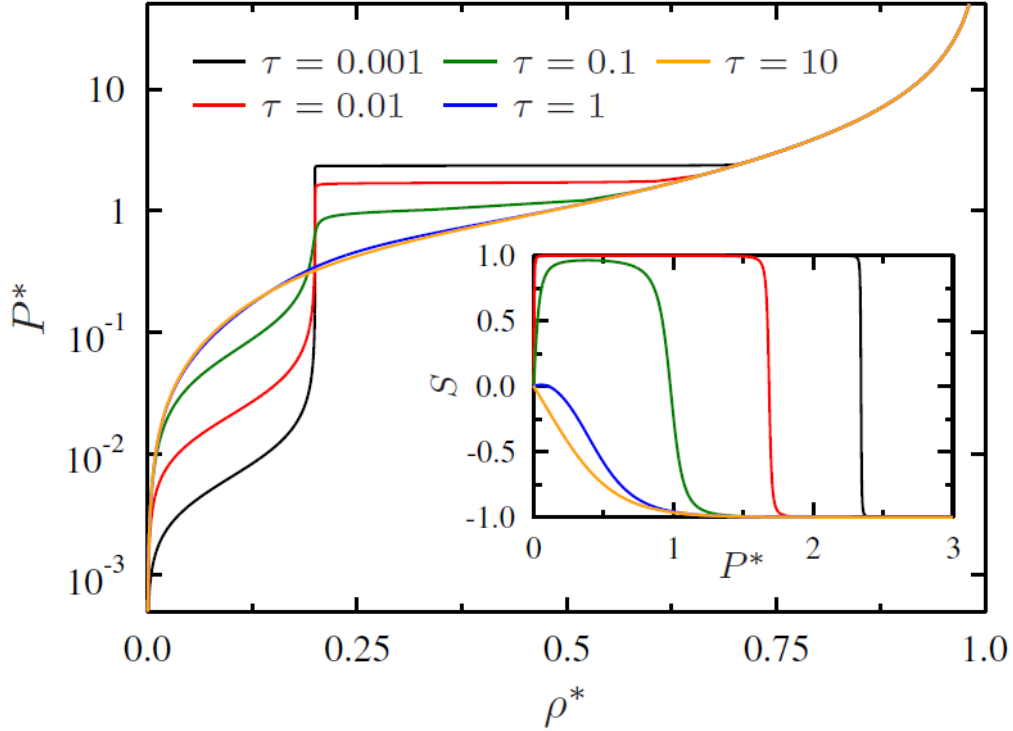


Figure 3. Equation of state of quasi-one-dimensional sticky hard rods in the pressure ($P^* = \beta PD$) vs. density ($\rho^* = \rho D$) plane. The inset shows the nematic order parameter (S) as a function of pressure. For all curves: $L/D=5$.

condition, which occurs at the cross point, we get the transition pressure in the following form

$$P_{-|}^* = \frac{\ln \alpha}{L/D - 1}. \quad (22)$$

Using this pressure, we can obtain the coexisting density of the horizontal structure from Eq. (18) and that of vertical one from $\beta P^* = \rho^* / (1 - \rho^*)$. As the transition pressure diverges with $\tau \rightarrow 0$, the transition densities goes to the close packing densities of horizontal and vertical structures, i.e. the phases with $\rho_{-}^* = \frac{1}{L/D}$ and $\rho_{|}^* = 1$ are in phase coexistence in the limit of $\tau \rightarrow 0$. Since the agreement between the level crossing approximation and the exact results improves with decreasing stickiness parameter, a first order phase transition occurs between the horizontal and the vertical structures in the limit of $\tau \rightarrow 0$.

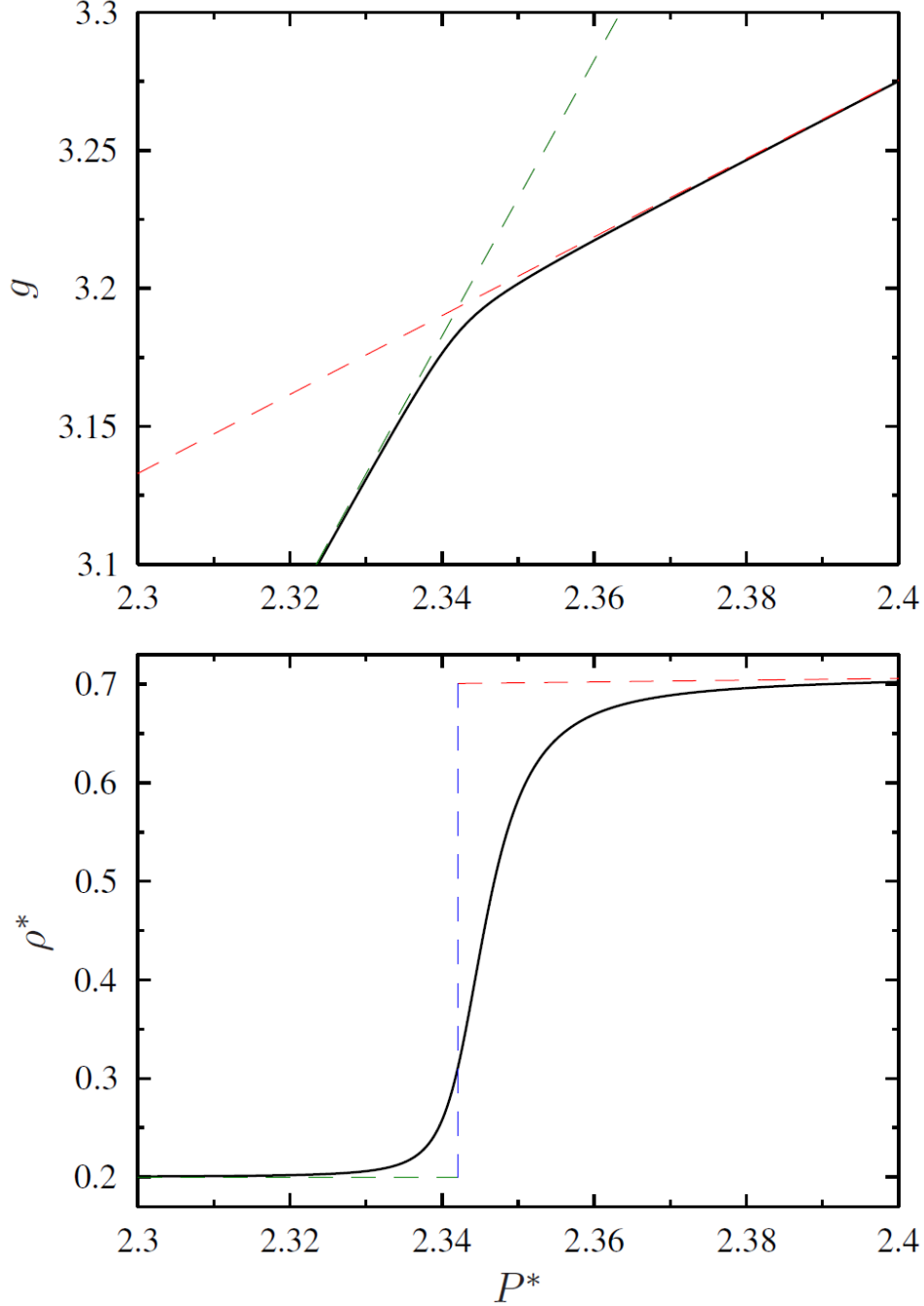


Figure 4. The effect of the level-crossing approximation on the Gibbs free energy (upper panel) and the equation of state (lower panel). The curves in the figure: $g = -\ln(\lambda)$ (continues), $g = -\ln(K_{--})$ (green dashed) and $g = -\ln(K_{|})$ (red dashed). The vertical blue dashed line connects the coexisting phases. The corresponding equation of states come from $1/\rho = dg/d(\beta P)$. For all curves: $L/D=5$ and $\tau=0.001$. The quantities are dimensionless: $\rho^* = \rho D$, $P^* = \beta P D$, and $g = \beta G/N$.

As the first order phase transitions satisfy the so called lever rule, the present sticky rod system should obey it in the limit of $\tau \rightarrow 0$, too. Let us assume that N^- particles in the volume V^- coexist with $N^|$ particles in the volume $V^|$, where $-$ and $|$ denote the horizontal and vertical phases, respectively. We mention that both phases are allowed to have particles with horizontal

and vertical orientations. Therefore, in general we can only say that the majority of the particles are horizontal in $-$ phase, and vertical in $|$ one. Moreover, the total number of particles (N) and the volume of system (V) satisfy $N = N^- + N^|$ and $V = V^- + V^|$ [56]. Then the volume rates $v^- = V^- / V$ and $v^| = V^| / V$ must obey $\rho = \rho^- v^- + \rho^+ v^+$, where $\rho = N/V$ is the total number density, $\rho^- = N^- / V^-$ and $\rho^| = N^| / V^|$ are the densities of coexisting phases. This is the so-called lever rule. Using $v^- + v^| = 1$ we can express v^- as a function of ρ as follows

$$v^- = (\rho - \rho^|) / (\rho^- - \rho^|), \quad (23)$$

where $\rho^- \leq \rho \leq \rho^|$. This shows that the volume fraction is linearly dependent on density. A similar formula can be derived for the number rates of the coexisting phases as

$$x^- = (1/\rho - 1/\rho^|) / (1/\rho^- - 1/\rho^|), \quad (24)$$

where $x^- = N^- / N$ is the fraction of particles in the phase $-$. In this case x^- depends linearly on $1/\rho$. In the case of level crossing approximation, Eqs. (23) and (24) are fulfilled exactly because there is no pressure value, where ρ is between ρ^- and $\rho^|$. In the exact transfer matrix calculations, we can assume that the coexisting densities are identical with the coexisting densities coming from the level crossing approximation. Moreover, it is quite feasible that the horizontal and vertical particles do not mix for $\rho^- \leq \rho \leq \rho^|$, i.e. $x^- \approx x_-$ is a reasonable approximation of the reality. To check the validity of the above assumptions we determine x_- as a function of $1/\rho$, where x_- and $1/\rho$ are the exact results of the transfer matrix method. As the volume fraction can be expressed as $v^- = \rho x^- / \rho^-$, v^- can be obtained in the biphasic region using $x^- \approx x_-$, where ρ^- is the results of level crossing approximation. To check the validity of the lever rule, we plot $v^- (x_-)$ as a function of $\rho (1/\rho)$ for sticky hard rods in Fig. 5. To see the deviation from the lever rule, Eqs. (23) and (24) are also presented using the level crossing approximation results for ρ^- and $\rho^|$. We can see that transfer matrix results get closer to the lever rule curves with decreasing τ . As the agreement between them is already very good at $\tau=0.001$, the collapse of lever rule curves and the transfer matrix results must happen in the limit of $\tau \rightarrow 0$. As an additional check of the lever rule, we calculated the fraction of interfacial regions ($x_{-|} + x_{|-}$), where a horizontal particle is the neighbour of a vertical particle [57]. We can see in Fig. 5 that number of horizontal and vertical neighbours goes to zero with decreasing stickiness parameter, i.e. $x_{-|} \rightarrow 0$ with $\tau \rightarrow 0$. This finding validates our assumption that $x^- \approx x_-$.

It is a well-known fact that the stickiness parameter of the sticky particles can be replaced with the second virial coefficient (B_2). In the system of 1D sticky hard rods, it can be shown that

$$B_2^* = B_2 / L = 1 - 1/\tau. \quad (25)$$

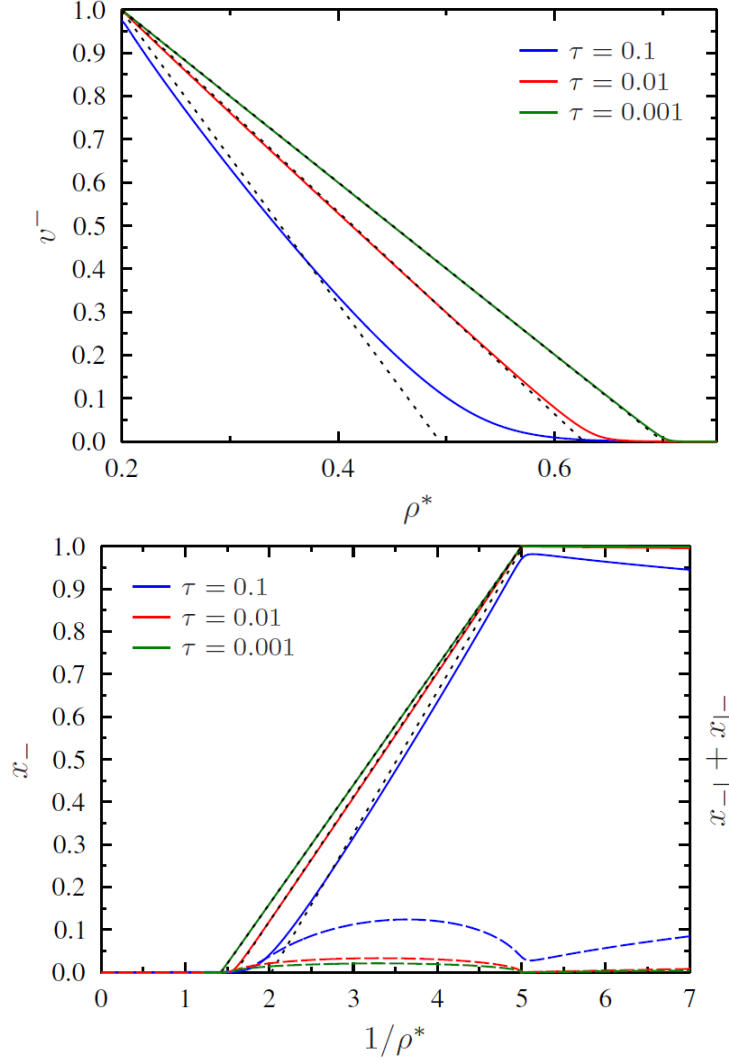


Figure 5. The check of the lever rule for the horizontal to the vertical structural transition of sticky hard rods. The volume rate of the horizontal order ($v^- = V^-/V$) as a function of density is shown in the upper panel, while the fraction of horizontal particles (x_-) and the fraction of horizontal and vertical pairs ($x_- + x_|$) are presented as a function of inverse density in the lower panel. The continuous curves corresponds to the exact results, while the dashed ones comes from the level-crossing approximation. The long dashed curves represent the fraction of horizontal and vertical pairs. For all curves: $L/D=5$.

Therefore the equation of state of sticky particles can be expressed as a function of packing fraction ($\eta = \rho L$) and B_2^* , i.e. $\beta PL = f(\eta, B_2^*)$. In three dimensions, it is found that the above results for hard spheres with short range attraction is also valid if the range of the attraction does not exceed about the 10 % percent of the particle's diameter [58, 59]. In addition to this, the resulting vapour-liquid binodal is universal in B_2^* vs. η plane, i.e. the binodals of different systems collapse into a single master curve for very short range attractions [60]. This is the so-called extended law of corresponding states (ELCS). We check whether our attractive rod systems follows the ELCS or not if B_2^* is kept fixed, but the range of the attraction (δ) is varied.

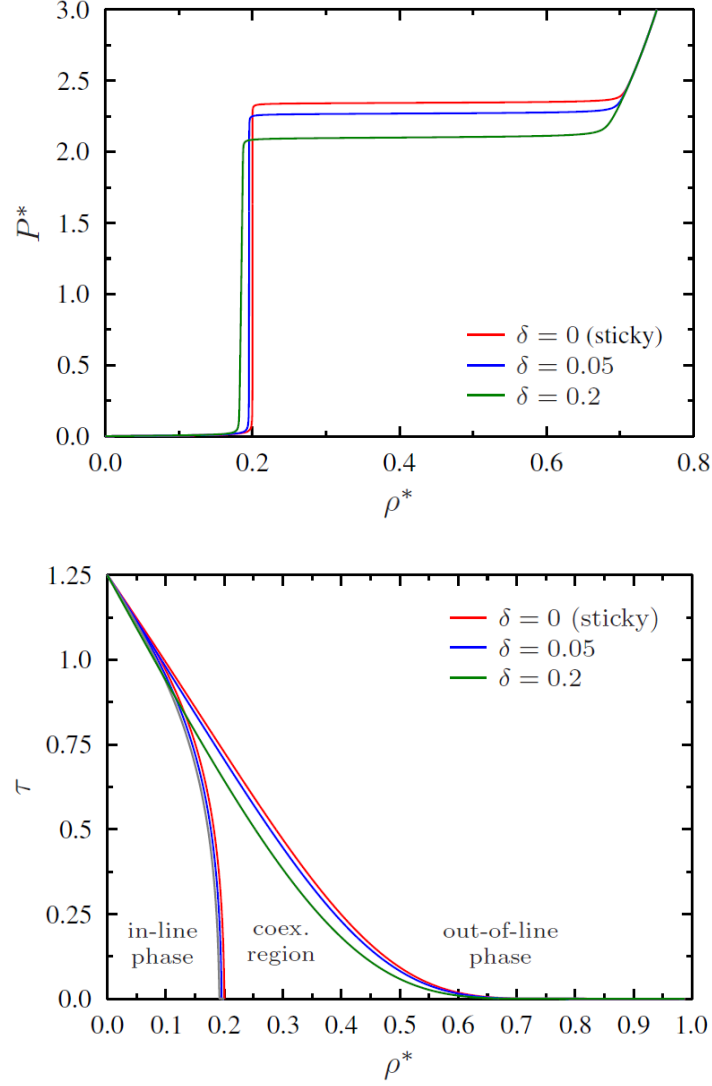


Figure 6. The equation of state and the level crossing phase diagram of the two-state attractive rods. For all curves: $L/D=5$ and $\tau=0.001$. The quantities are dimensionless: $\rho^* = \rho D$ and $P^* = \beta P D$.

Our transfer matrix results using Eqs. (8), (11) and (12) for the equation of state is shown in Fig. 6. We can see that the increasing δ does not change the shape of the curves, but it lowers the pressure of the structural transition between horizontally and vertically ordered structures. Regarding the equation of state, we can see that it is independent of δ in the vertical ordering as the high density phase behaviour depends on $K_{||}$ matrix element, which does not depend on δ . However, this is not true in the horizontal structure, because K_{--} determines the phase behaviour, which depends on δ (see Eq. (8)). Therefore, it is not surprising that the equation of state depends on δ , too. In the strict sense, this means that the ELCS is not valid for 1D square-well fluid, because the effect of δ cannot be built into B_2^* and $\beta P L = f(\eta, B_2^*, \delta)$. The δ dependence of the pressure changes the horizontal-vertical phase coexistence curve coming from the level crossing approximation. This can be seen clearly in Fig. 6, where the phase diagram is presented in τ vs. η plane. The lack of the collapse of the curves indicates that B_2^* vs. ρ^* does not form a master curve for 1D particles with short range attractions. We can say

that the details of short range pair interactions cannot be built into the second virial coefficient to describe the phase behaviour of 1D systems. However, the difference between the curves is quite small, when $\delta < 0.05$.

Conclusions

We have studied the equilibrium phase behaviour of the q1D system of hard rectangles with two attractive sites at the ends. Due to the presence of first-neighbour interactions only, the transfer matrix method provides exact results for the ordering properties and the equation of state. Using this method, the well-known Tonks equation can be reproduced for 1D hard rods without attractive sites and vertical orientational freedom [15]. Adding attractive sites to the rectangles, the phase behaviour is changed as the particles associate and form chains. However, the short range interactions cannot to produce vapour-liquid phase separation in accordance with the van Hove's theorem [19, 20]. The situation changes dramatically with the inclusion of one extra out-of-line orientational freedom, i.e. when the particle's orientation can be both horizontal and vertical, because the entropy favours the vertical ordering, while the association energy the horizontal one. The competition between the energy and the entropy gives rise to a structural change between horizontally and vertically ordered phases, which becomes more pronounced as the attraction is stronger. The contribution of the attraction can be controlled by the stickiness parameter τ , which is inversely proportional to the attractive part of the second virial coefficient, i.e. $\tau \rightarrow 0$ corresponds to an infinitely strong attraction. It is found in the limit of $\tau \rightarrow 0$ that the horizontal structure survives up to the close packing density of the horizontal order, which is in phase coexistence with a vertical structure. Moreover, the purely vertical structure exist only in the close packing limit, where the pressure is infinite. It is important to emphasize that the horizontal and vertical particles do not mix in the two phase region as the lever rule becomes exact and the fraction of neighbouring particles with different orientations goes to zero if $\tau \rightarrow 0$. Moreover, the density gap between the horizontal and vertical structures widens with increasing aspect ratio of the rectangle. In the limit of $L/D \rightarrow \infty$ and $\tau \rightarrow 0$, the horizontal order exist only at the vanishing density, while the vertical one at the close packing one. Therefore the validity range of the lever rule extends for the whole density range in this special limit. Note that the van Hove's theorem is only violated in the limit of $\tau \rightarrow 0$, where the off-diagonal elements of the transfer matrix become negligible with respect to the diagonal ones. It is interesting that there is no true phase transition at any nonzero value of τ , but a structural change happens from the horizontal ordering to the vertical one with increasing density. This structural change is reminiscent of a first order phase transition as the pressure has a very weak density dependence in the density region, which is bounded by the level crossing coexisting densities. The limiting first order phase transition is not terminated by a critical point, which suggest that the nature of this phase transition is different from the vapour-liquid one. Therefore it may be related to fluid-solid transitions occurring in higher dimensions, where the fluid-solid transition never terminates in a critical point.

We have also tested the validity of the extended law of corresponding state in our q1D system, since this law is devised originally for three dimensional spherical particles with short range attractions [60]. In contrast to three dimensional systems, where no exact results are

available to check this empirical law, the equation of state can be determined exactly in 1D systems with short range attractions. We have found that horizontal rectangles with two attractive sites do not obey this law, because the equation of state depends on the range of the attraction at given values of the density and the second virial coefficient. The deviation in the pressure vs. density curves can be quite big in the vicinity of the horizontal close packing densities as the attraction range is increased. This can be the reason why this law can be used only for vapour-liquid phase transition in higher dimensions. However, this law can be applied in one dimension, too, if the density is low. This can be also seen in the level crossing phase diagram of our system, where the phase boundaries move with the range of the attraction. Generally speaking, we can say that the extended law of corresponding state is approximate in all physical dimensions and valid only in the sticky limit [55].

Even though, our study is restricted to the two-state orientational model, which may exaggerate the change of the nematic order parameter upon increasing the pressure, the competition between the association energy and the entropy survives in the continuum limit of the orientation, which result in a horizontal-to-vertical structural transition. For example, the hard needles prefers the ordering along the vertical direction with increasing pressure and exhibit weaker nematic ordering in the continuum limit than in the 2-state model [25]. No doubt, this is due to the randomizing effect of the orientational entropy, which has higher contribution in the continuum limit. Therefore it is quite feasible that the structural change occurs at higher pressure in the case of freely rotating rectangles, because both the orientational entropy and association energy are against the vertical orientational order.

We believe that our model system is not only interesting for its equilibrium phase properties, but it may serve as a good toy model to study the jamming properties and the glassy behaviour of q1D systems. For example, the system of freely rotating hard rectangles exhibit jamming at the close packing because the orientational correlation length is diverging [29]. The two-state model of hard rectangles in the presence of aligning external field shows a hysteresis in the equation of state and a two-step decay is observed in the orientational persistence, which are typical glassy behaviours [31]. As both the attractive sites and the aligning external field forces the rectangles to be horizontal, we expect similar glassy behaviour in the attractive hard rectangle model, too. We leave the issues of jamming and glass formation of the present system for future studies.

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