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ONE-DIMENSIONAL MODELS OF ANISOTROPIC FLUIDS*

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INTRODUCTION

Equilibrium properties of fluids of approximately spherical molecules can be adequately described over a wide range of temperatures and densities by the classical statistical mechanics of point particles interacting *via* spherical pair potentials. The structure of these fluids can be calculated (away from phase transitions) fairly easily and accurately *via* various relatively well-understood approximation schemes.[1] The situation is less satisfactory for highly nonspherical molecular fluids; in these systems, particles have to be specified not only by the position of the center of mass, but also by internal coordinates. While many approximate schemes have been suggested for such systems, their assessment suffers from the unavailability of accurate experimental or computer simulation data, particularly for the full pair correlation function, against which they can be tested.[2,3] It is the aim of this paper to seek some such comparison test by considering a situation in which the fluid is confined to a very narrow channel. This case, while very far from typical, has the advantage that it can be solved exactly for simple model systems. It is our choice of solvable models that nevertheless exhibit some interesting behavior that distinguishes our work from more "realistic" one-dimensional model systems and from models involving long-range interactions considered and studied elsewhere.[4] We hope that our simple analytic answers will make it possible to identify those aspects which extend to less-restricted systems and to use them to recognize and develope better approximations.

Consider a situation in which the particles of a fluid are restricted to a cylinder with a diameter less than twice their minimal hard core diameter. Then the particles cannot change their order. If the longitudinal particle location is specified by z_i and the transverse location by $\mathbf{x}_i$, then we can assume that $z_1 < z_2 < \cdots z_N$ and a transfer operator analysis becomes feasible.[6] The number of particles that particle i can interact with depends upon the range of the interaction potential. In particular, if i can interact only with $i - 1$ and $i + 1$, the problem may become analytically tractable.

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In the above, there is no formal distinction between the transverse coordinates and any internal degrees of freedom a particle may possess. With this in mind, we shall consider here, for definiteness, only systems composed of "hard molecules" whose centers are confined to lie on a line. The orientation of the particles will be specified by the unit vector ω with a given *a priori* weight, $m(\omega)d\omega = d\nu(\omega)$. This will permit us to consider discrete orientations or other restrictions on the range of ω, *e.g.*, ω may be forced to lie on the unit circle, in which case $\omega \rightarrow \theta \in [0,2\pi]$. In addition to the hard-core interaction, there may also be a residual, soft, angle-dependent, finite range potential such that the total interaction, $\phi(z-z'; \omega, \omega')$, extends only to nearest-neighbor particles.

The outline of this paper is as follows. In the next section we recall briefly the pressure ensemble formalism for one-dimensional systems, leading to the transfer matrix concept. We note a certain inequality, valid when the transfer matrix is symmetric, between the exact chemical potential and that obtained from a "spherical-ized" interaction. We then consider interactions for which the problem is easily solvable, including a limit in which the system undergoes a phase transition. In the next-to-last section we consider discrete orientations, which can be regarded equivalently as representing a mixture of different species with either additive or nonadditive diameters.

General Formalism

It will be convenient to use periodic boundary conditions in which particle 0 is fixed at $z_0 = 0$, particle N at $z_N = L$, and these two particles are identified, $\omega_0 = \omega_N$. (The boundary conditions will be of no consequence in the thermodynamic limit.) The configurational partition function for this system in the isobaric ensemble is equal to

$$\mathrm{Tr}\, Z_p^N \equiv \int_\Omega d\nu(\omega)\, Z_p^N(\omega, \omega), \tag{1}$$

where Ω is the internal space available per particle and the positive transfer operator, Z_p, is defined by

$$Z_p(\omega, \omega') = \int_0^\infty e^{-\beta\phi(z;\omega,\omega')}\, e^{-\beta p z} dz. \tag{2}$$

Going to the thermodynamic limit yields the chemical potential

$$\mu = -\frac{1}{\beta} \ln \lambda_{\max}(Z_p), \tag{3}$$

where $\lambda_{\max}$ is the maximum eigenvalue of Z_p. We also have

$$\lambda_{\max} = \int\int \psi^+(\omega)\, \psi(\omega')\, Z_p(\omega,\omega')\, d\nu(\omega)\, d\nu(\omega'), \tag{4}$$

where $\psi(\omega)$ is the maximal eigenfunction and $\psi^+(\omega)$ is the maximal adjoint eigenfunction of $Z_p(\omega,\omega')$ (which need not be symmetric) satisfying $\psi(\omega) \geq 0$, $\psi^+(\omega) \geq 0$,

$$\int \psi^+(\omega)\, \psi(\omega)\, d\nu(\omega) = 1. \tag{5}$$

The integrand in (5) specifies the fraction of particles in $d\omega$. The density, n, as a

function of pressure, is given by

$$\frac{1}{n} = -\frac{1}{\beta}\frac{\partial}{\partial p}\ln \lambda_{\max}. \tag{6}$$

A popular approximation for anisotropic molecules is to average the Boltzmann factor separately over its internal variables, ω and ω'. According to (2), this entails the replacement of $Z_p(\omega,\omega')$ by $\overline{Z}_p$,

$$\overline{Z}_p = \int\int Z_p(\omega,\omega')\, d\nu(\omega)\, d\nu(\omega')/|\Omega|^2, \tag{7}$$

a constant in ω and ω' whose maximum eigenvalue is $\bar{\lambda}_{\max} = |\Omega|\overline{Z}_p|\Omega| = \int_\Omega d\nu(\omega)$. This is obtainable from (4) by the substitution $\psi(\omega) = \psi^+(\omega) \to |\Omega|^{-1/2}$. It follows that, for symmetric Z_p, $\bar{\lambda}_{\max} \leq \lambda_{\max}$; hence, that $\bar{\mu}(p) \geq \mu(p)$. The error in $\lambda_{\max}$ is clearly second order in the ω-depencence of $e^{-\beta\phi}$. Whether this is small or not depends very much upon the nature of ϕ, as we shall soon see.

Hard Discs with Anisotropic Interactions

We will now specialize to a case in which an explicit solution can be found, allowing us to study the validity of approximations such as (7). We consider hard discs of diameter a with centers on the z-axis. The internal degree of freedom is the uniformly weighted angle, θ, of some identified point on the disc. We further imagine an adhesive coat on the circumference of each disc with a density proportional to $g(\theta)$, *i.e.*, the interaction Boltzmann factor will be taken to be

$$e^{-\beta\phi(z;\theta,\theta')} = e^{-\beta\phi_h(z)} + \delta(z-a)\, g(\theta)g(\theta'+\pi), \tag{8}$$

where ϕ_h is the hard disc interaction potential, $\phi_h(z) = \infty$ for $|z| < a$, zero otherwise. This leads to the transfer matrix

$$Z_p(\theta,\theta') = \frac{e^{-\beta pa}}{\beta p} + e^{-\beta pa}\, g(\theta)\, g(\theta'+\pi), \tag{9}$$

which will be symmetric iff $g(\theta) = g(\theta+\pi)$; of course, we always have $g(\theta) = g(\theta+2\pi)$.

The matrix Z_p of (9) is of rank 2. It therefore has two nonzero eigenvectors, which take the form

$$\psi(\theta) = b_1 + b_2\, g(\theta) \text{ and } \psi^+(\theta) = b_1 + b_2 g(\theta+\pi). \tag{10}$$

Inserting this in the equation

$$\int_0^{2\pi} Z_p(\theta,\theta')\,\psi(\theta')d\theta' = \lambda\psi(\theta),$$

we find that the maximum eigenvalue is given by

$$\lambda_{\max} = \frac{\pi}{\beta p}\, e^{-\beta pa}\,[1 + \beta p\overline{g}\overline{g}_+ + ((1-\beta p\,\overline{g}\overline{g}_+)^2 + 4\beta p\overline{g}^2)^{1/2}],$$

where

$$\bar{g} = \frac{1}{2\pi}\int_0^{2\pi} g(\theta)\mathrm{d}\theta, \qquad \overline{gg}_+ = \frac{1}{2\pi}\int_0^{2\pi} g(\theta)\,g(\theta+\pi)\mathrm{d}\theta. \tag{11}$$

For purposes of comparison, $\bar{\lambda}_{\max}$ of (7) here becomes

$$\bar{\lambda}_{\max} = 2\,\frac{\pi}{\beta p}\,e^{-\beta p a}\,(1+\beta p\bar{g}^2), \tag{12}$$

whose difference from (11) may be measured by the covariance

$$C = \overline{gg}_+ - \bar{g}^2. \tag{13}$$

Let us consider two extreme cases of (9). The first is $\overline{gg}_+ = 0$, but $\bar{g}$ is finite, as, *e.g.*, with a single glue spot,

$$g(\theta) = 2\pi\bar{g}\delta(\theta), \qquad 0 \le \theta < 2\pi. \tag{14}$$

Here, as the density increases, we would expect the discs to ultimately stick together as dimers. Indeed, this negative covariance case leads to such a result quantitatively, for (11) now yields

$$n = \beta p \Big/ \left(1 + \beta p a - \frac{2\beta p\bar{g}^2}{1 + 4\beta p\bar{g}^2 + \sqrt{1+4\beta p\bar{g}^2}}\right). \tag{15}$$

At small βp, $n \simeq \beta p/[1+\beta p(a-\bar{g}^2)]$, or

$$\beta p \simeq \frac{n}{1-n(a-\bar{g}^2)}, \qquad \beta p a \ll 1. \tag{16}$$

The term $a - \bar{g}^2$ in the denominator of (16) may be considered an effective reduction of the core diameter. But, at large βp, we have, instead, $n = \beta p/(1/2 + \beta p a)$, or

$$\beta p = \frac{n/2}{1-(n/2)\,2a}, \qquad \beta p a \gg 1, \tag{17}$$

a gas of half the density but double the diameter, *i.e.*, dimers. The corresponding result from (12),

$$\bar{n} = \frac{\beta p(1+\beta p\,\bar{g}^2)}{(1+a\beta p(1+\beta p\,\bar{g}^2))},$$

becomes

$$\beta\bar{p} = \begin{cases} \dfrac{n}{1-na}, & \text{small } \beta\bar{p}a, \\[2ex] \dfrac{1}{\bar{g}}\,(n/1-na)^{1/2}, & \text{large } \beta\bar{p}a. \end{cases} \tag{18}$$

Equation 18 shows too high a pressure reduction near close packing.

The second extreme case is given by $\bar{g} = 0$, $\overline{gg}_+ > 0$. Since $g \ge 0$, this is only satisfied as a limiting case. For example, for w of finite support, let us consider the

symmetric case

$$g_\lambda(\theta) = \left(\frac{\lambda}{2}\right)^{1/2}\left[\frac{1}{\lambda}w\left(\frac{\theta}{\lambda}\right) + \frac{1}{\lambda}w\left(\frac{\theta+\pi}{\lambda}\right)\right], \qquad 0 \le \theta < 2\pi.$$

Then, as $\lambda \to 0$, $\bar{g}_\lambda \to 0$ and

$$\overline{gg}_+ \to \int w^2(\alpha)\mathrm{d}\alpha. \tag{19}$$

Here two glue spots of increasing amplitude and decreasing total strength are located diametrically opposite so that, when the spots are perfectly aligned, a polymer forms. In this case, (6) reduces to

$$n = \begin{cases} \dfrac{\beta p}{1+\beta p a}, & \beta p < 1/\overline{gg}_+, \\ \dfrac{1}{a}, & \beta p > 1/\overline{gg}_+, \end{cases} \tag{20}$$

so that

$$\beta p = \begin{cases} \dfrac{n}{1-na}, & n \le \dfrac{1}{a+\overline{gg}_+}, \\ \dfrac{1}{\overline{gg}_+}, & \dfrac{1}{a+\overline{gg}_+} < n < \dfrac{1}{a}, \\ \infty, & n > \dfrac{1}{a}. \end{cases} \tag{21}$$

In other words, one has pure cores up to a critical density, then a flat isotherm leading to the close-packed phase. This example of a first-order phase transition—albeit a degenerate one—in a one-dimensional system with short-range forces does not contradict the Van Hove theorem,[6] since it is only a limiting case. Indeed, if $\bar{g} > 0$, no matter how small, the corners on the p-v curve are rounded and the isotherm is no longer perfectly flat (FIGURE 1). However, the transition is unusual, so one is not surprised to find an approximation such as (7) missing it totally and yielding a purely hard core result throughout. And that is precisely the point: The qualitative effects associated with angular structure demand special care if they are to be picked up adequately.

To examine the system a bit further, we shall look at the angular distribution of the model, (9). This is given, in general, by

$$f(\omega) = \psi(\omega)\,\psi^+(\omega). \tag{22}$$

In the case considered here, b_2/b_1 of (10) is a measure of the anisotropy of the angular distribution; this is given explicitly by

$$2\frac{b_2}{b_1} = [(1-\beta p\,\overline{gg}_+)^2 + 4\beta p\,\bar{g}^2]^{1/2} - (1-\beta p\,\overline{gg}_+). \tag{23}$$

Thus, for the cases we have examined, $\overline{gg}_+ = 0$ gives

$$\frac{b_2}{b_1} = \frac{1}{2}\left(\sqrt{1 + 4\beta p\bar{g}^2} - 1\right); \tag{24}$$

the ratio rises steadily but weakly with increase in pressure. On the other hand, $\bar{g} = 0$ gives $b_2/b_1 = 0$ in the low-density phase but $b_2/b_1 = \beta p\ \overline{gg}_+ - 1$ in the close-packed phase. The transition is not as strong as a standard order-disorder transition, since it is easy to show that $\lim_{m\to\infty} < \omega_j \cdot \omega_{j+m} > \longrightarrow 0$ in all states.

An interesting variation on this model corresponds to having m glue spots, $m > 2$, on each disc. This might permit the system to retain suitable disorder even after undergoing a transition—there could, in fact, be several transitions. It may also be possible to investigate systems of this type in high dimensions.

Anisotropic Hard Cores

A anisotropy different from that provided by the model, (9), occurs when the shape itself is not isotropic, *e.g.*, an ellipsoidal hard core. The essence of the situation is the change in exclusion volume as a function of orientation; for this purpose, it should

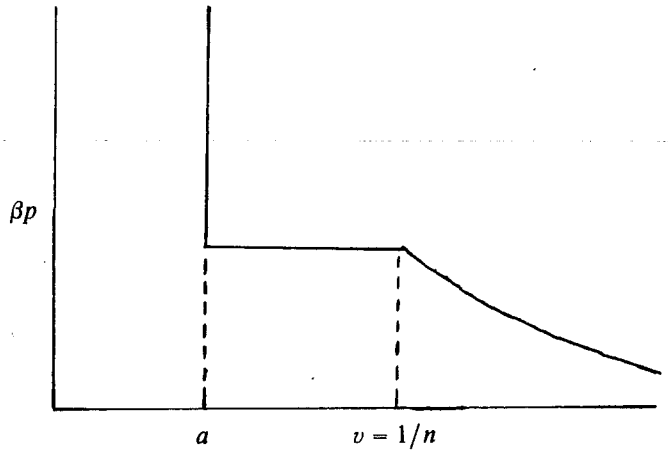

Figure 1.

suffice to consider a set of discrete orientations: $d\nu(\omega)$ is the sum of delta functions at orientational angles $\theta_\alpha = \alpha\pi/m$ ($\alpha = 0, \ldots m - 1$), where we have assumed particles symmetric about their centers, so that θ runs from 0 to π. Let the exclusion distance for adjacent particles with angled θ_α and θ_γ be $a_{\alpha,\gamma}$; then

$$Z_p(\alpha,\gamma) = (\beta p)^{-1}\, e^{-\beta p a_{\alpha\gamma}}. \tag{25}$$

In the additive diameter case, $a_{\alpha,\gamma} = a_\alpha + a_\gamma$, the transfer matrix is identical, after some relabeling, to a noninteracting m-component spin system on a one-dimensional

lattice in a general external field. This gives at once

$$\lambda_{\max} = \frac{1}{\beta p} \Sigma_\alpha e^{-\beta p a_{\alpha,\alpha}}. \tag{26}$$

The density then becomes

$$n = \frac{\beta p}{1 + \beta p\, \bar{a}}, \qquad \beta p = \frac{n}{1 - n\bar{a}}, \tag{27}$$

with

$$\bar{a} = \frac{\Sigma a_{\alpha\alpha} e^{-\beta p a_{\alpha\alpha}}}{\Sigma e^{-\beta p a_{\alpha\alpha}}} = \Sigma a_{\alpha\alpha} n_\alpha / n, \tag{28}$$

n_α/n being the fraction of particles with angle θ_α. Equation 28 gives the properly weighted average diameter, which reduces in the low- and high-pressure limits to

$$\bar{a} \sim \int d\nu_\alpha\, d\nu_\gamma\, a_{\alpha\gamma} / |\Omega|^2, \qquad |\Omega| = m, \quad \text{for} \quad \beta p \bar{a} \ll 1$$

and

$$\bar{a} \sim \min_\alpha a_{\alpha\alpha}, \quad \text{for} \quad \beta p \bar{a} \gg 1. \tag{29}$$

This is quite different from averaging the Boltzmann factor, which leads to an effective interaction that is not purely hard core. The two procedures may give quite different answers, except possibly for the case of approximately equal diameters. In three dimensions, too, "volume and surface" averaging obtained from the solution of the Percus-Yevick equation yields good results for the equation of state of additive hard spheres.[7]

In the more realistic nonadditive case, the situation is more complicated. For $m = 2$, corresponding to particles with two orientations, one finds

$$\beta p\, \lambda_{\max} = (e^{-\beta p a_{11}} + e^{-\beta p a_{22}}) + \frac{1}{2}[(e^{-\beta p a_{11}} - e^{-\beta p a_{22}})^2 + 4e^{-2\beta p a_{12}}]^{1/2}, \tag{30}$$

so that

$$n = \left[\frac{1}{\beta p} + a_{12} + \Delta\right]^{-1},$$

where

$$\Delta = \left(\frac{\alpha_1}{\alpha_1 + \alpha_2}\Delta_1 + \frac{\alpha_2}{\alpha_1 + \alpha_2}\Delta_2\right)\frac{l_1 + l_2 + s - 4/s}{l_1 + l_2 + s},$$

$$\alpha_1 = l_1\left(1 + \frac{l_1 - l_2}{s}\right), \qquad \alpha_2 = l_2\left(1 + \frac{l_2 - l_1}{s}\right), \qquad s^2 = (l_1 - l_2)^2 + 4, \tag{31}$$

$$l_1 = e^{-\beta p \Delta_1}, \qquad l_2 = e^{-\beta p \Delta_2}, \qquad \Delta_1 = a_{11} - a_{12}, \quad \text{and} \quad \Delta_2 = a_{22} - a_{12}.$$

There is now a large repertoire. For small βp, $\Delta = \frac{1}{4}(\Delta_1 + \Delta_2)$. As $\beta p \to \infty$, $\Delta \to \Delta_2$ when $a_{11} > a_{12} > a_{22}$ or $a_{12} > a_{11} > a_{22}$, but $\Delta \to 0$ when $a_{11} > a_{22} > a_{12}$.

The analysis of (31) is facilitated by supposing that $a_{11} = a_{22} \neq a_{12}$. Equation 31 then reduces to

$$\frac{1}{n} = \frac{1}{\beta p} + \frac{1}{1 + e^{\beta p \Delta}} a_{11} + \frac{e^{\beta p \Delta}}{1 + e^{\beta p \Delta}} a_{12}, \qquad \Delta = a_{11} - a_{12}. \tag{32}$$

Now, if $a_{11} < a_{12}$ or $\Delta < 0$, then the mean exclusion volume as $\beta p \to \infty$ is $a_{11} = a_{22}$, implying a phase separation in which the proportion of 1-2 contacts approaches zero. On the other hand, if $a_{12} < a_{11}$ or $\Delta > 0$, then this volume approaches a_{12}, so there must be an alternation of orientations, an asymptotoic antiferromagnetic ordering. Both effects are precisely as expected: (**32**) again has a form suggestive of a hard rod system with an average diameter.

Concluding Remarks

It is clear that models with internal degrees of freedom are indistinguishable from interconvertible mixtures: The parameter θ can denote a particle type rather than a physical angle. Thus, our analysis in the preceding section applies equally well to a mixture of hard rods at equal chemical potential, with both additive and nonadditive diameters.[8]

It is interesting to ask what the analogy of the transition, (**19–21**), becomes in the mixture format. We may choose

$$Z_p(\alpha, \gamma) = \frac{e^{-\beta p a}}{\beta p}(1 + \beta p\, g_\alpha\, g_\gamma), \qquad \alpha = 0, \ldots m - 1. \tag{33}$$

This leads to

$$\gamma_{\max} = \frac{m}{2\beta p}\, e^{-\beta p a}\{(1 + \beta p \bar{g}^2) + [1 - \beta p \bar{g}^2)^2 + 4\beta p \bar{g}^2]^{1/2}\}, \quad \text{where} \quad \bar{g} = \frac{1}{m}\Sigma g_\alpha. \tag{34}$$

The condition $\bar{g} = 0$, $\bar{g}^2$ finite is now satisfied if

$$g_\alpha = (\bar{g}^2)^{1/2}\,(m)^{1/2}\,\delta_{\alpha,0} \tag{35}$$

and $m \to \infty$. Thus, the mixture interpretation is that of a polydisperse system of hard rods in which only one component, $\alpha = 0$, interacts adhesively with itself. In this case, the analysis of (**20–21**) is simply reproduced.

We saw that even the primitive example of a one-dimensional fluid with angular internal variables can elicit behavior involving collective angular relationships and that this is mirrored by polydisperse one-dimensional mixtures. These considerations may serve to check on approximations used for real molecular systems, as well as to suggest others. We expect to employ them in such a fashion.

It should be noted that the singular close-packed nature of the condensed phase in (**21**) is an artifact of the 0 range of the glue spots in (**8**). If $\delta(z - a)$ is replaced by $w(z - a)$, the development goes through unchanged in form, except for the substitutions $e^{-\beta p a} \to e^{-\beta p a}\,\tilde{w}(\beta p)$, $\beta p \to \beta p\,\tilde{w}(\beta p)$, where $\tilde{w}$ is the Laplace transform of w. Thus, *e.g.*, (**20**) is replaced by the more realistic

$$n = \begin{cases} \dfrac{\beta p}{1 + \beta p a} & \dfrac{1}{\overline{gg}_+} > \beta p \tilde{w}(\beta p), \\[2ex] \dfrac{1}{a - \tilde{w}'(\beta p)/\tilde{w}(\beta p)} & \dfrac{1}{\overline{gg}_+} < \beta p \tilde{w}(\beta p). \end{cases} \tag{36}$$

It may also be noted that, in this case, a nonlimiting $\bar{g} = 0$ can be achieved with g negative in part if $w(z - a) = 0$ for $z < a$ and $w_{\max} g(\theta) g(\theta') > -1$, all θ, θ', but then $\beta p \tilde{w}(\beta p) \overline{gg}_+ < 1$, precluding the possibility of a transition.

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Summary

We used transfer matrix techniques to calculate the equilibrium properties of model classical systems with orientation-dependent pair potentials confined to a narrow channel. The results, including phase transitions in some limiting cases, were compared with those obtained from some sphericalized approximations.

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