Equation of state for hard-sphere fluids with and without Kac tails

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(Received 29 October 2007; accepted 19 March 2008)

We propose a simple derivation of the one-dimensional hard-rod equation of state, with and without a Kac tail (a long-range and weak potential). The case of hard spheres in higher dimension is also addressed, and we recover the virial form of the equation of state in a direct way.

[DOI: 10.1119/1.2908182]

I. INTRODUCTION

Much effort in the 19th century was aimed at explaining the deviation of the equation of state of dense gases and liquids from the ideal gas law.[1] Although the machinery of statistical mechanics offers a consistent framework for calculating the equation of state,[2,3] very few interacting systems have an equation of state that can be written in closed form.

The hard-rod fluid (also called Tonks or Jepsen gas[4,5]) is a notable exception. For N rods with a distribution of lengths $\{\ell_i\}_{1\le i\le N}$, enclosed in a line of total length L, the pressure P can be written as[4]

$$P = \frac{\rho kT}{1-\eta}, \tag{1}$$

where T is the absolute temperature, $\rho = N/L$ is the density, $\eta = \Sigma_i \ell_i / L$ is the line covering fraction (so that η/ρ is the mean rod length), and k is Boltzmann's constant. Several equilibrium and nonequilibrium quantities can also be calculated,[5] and the model provides a reference system for perturbative treatments, one of which we will address in the following with the inclusion of a Kac potential of interaction between the particles.[6,7]

In textbooks[2,3] as well as in the original papers,[4,8–10] the derivation of Eq. (1) is not straightforward. The purpose of this paper is to propose an alternative argument which relies on simple physical considerations rather than partition functions and mathematical computations. When applied to systems of higher dimensions $d>1$, the argument provides the exact equation of state of a hard-sphere fluid, which, however, cannot be written in closed form as an explicit function of the density.[11]

II. EQUATION OF STATE OF HARD-ROD AND HARD-SPHERE FLUIDS

We begin with the one-dimensional case (hard rods). To achieve our goal of calculating the pressure, we consider several related "Gedanken experiments." We first note that upon rescaling all lengths in the system by a factor of $1+\epsilon$,

$$\ell_i \to (1+\epsilon)\ell_i \text{ for } 1 \le i \le N, \quad L \to (1+\epsilon)L, \tag{2}$$

the reversible work δW_{total} associated with this rescaling reduces to its ideal gas contribution because excluded volume is irrelevant in this transformation. (It is essential to also rescale the box length L.) Only the ideal entropy of mixing is affected by this rescaling. We have

$$\delta W_{\text{total}} = -\rho kT\delta L, \tag{3}$$

where $\delta L = \epsilon L$ is the total length change. Equation (3) holds beyond hard-body interactions and applies whenever the system is governed by a unique length scale.[12] It would in particular hold for Lennard-Jones interactions. For $\delta L > 0$, the work δW_{total} is negative. If only the box length is expanded, the work δW_{total} done on the gas is negative. The additional particle expansion considered here amounts to a positive contribution to δW_{total}, which is smaller in magnitude than the previous one. The total work (sum of the two aforementioned contributions) is negative, as we will show explicitly in the following.

We perform the rescaling in Eq. (2) in two steps and calculate separately the reversible work required: (a) The rod sizes are slowly and sequentially rescaled one at a time:

$$\ell_1 \to (1+\epsilon)\ell_1, \ell_2 \to (1+\epsilon)\ell_2 \ldots . \tag{4}$$

(b) The box size is expanded $L \to (1+\epsilon)L$.

In step (a) any rod that is expanded behaves as a confining wall (piston) which "pushes" the fluid so that the work needed to rescale particle i is $P\delta\ell_i = P\epsilon\ell_i$ (we will comment further on this fact). Consequently, the work needed to perform step (a) is

$$\delta W_a = \sum_{i=1}^{N} P\delta\ell_i = P\delta L_p, \tag{5}$$

where L_p is the total length occupied by the rods ($\delta L_p = \eta\delta L$). For step (b) the work is given by

$$\delta W_b = -P\delta L. \tag{6}$$

The sum of both contributions, $\delta W_{\text{total}} = \delta W_a + \delta W_b$, is

$$-\rho kT\delta L = P\eta\delta L - P\delta L, \tag{7}$$

which implies that

$$P = \frac{\rho kT}{1-\eta}, \tag{8}$$

the exact result in one dimension. We stress that irrespective of the sign of the scaling parameter ϵ, the moves considered in steps (a) and (b) do not produce overlaps between particles nor between particles and the confining boundaries, in the same way as a moving boundary like a piston does not lead to overlaps (whenever two particles come in contact, the expanding rod "pushes" away its neighbor). We also note that from the form of the equation of state Eq. (8) all the virial coefficients are unity.[13]

We follow the same line of reasoning, and investigate the equation of state of hard spheres in dimensions $d>1$. We still have

$$\delta W_{\text{total}} = \delta W_a + \delta W_b = -\rho kT\delta V, \tag{9}$$

where V is now the volume of the system, and $\delta W_b = -P\delta V$. However, δW_a is not as straightforwardly related to the pressure as in Eq. (5). To obtain its form we introduce the pair correlation function $g(r)$.[3,11] For simplicity, we consider only the monodisperse case where all particles have the same diameter σ. The force per unit area felt by a given particle is of kinetic origin and is $\rho kTg(\sigma)$. Because a particle is surrounded by an excluded volume sphere of diameter 2σ, where no other particle's center may be, we can write the work needed to expand σ to $\sigma+\delta\sigma$ as

$$\delta W_{\sigma\to\sigma+\delta\sigma} = \rho kTg(\sigma)\delta V_{\text{sweep}}, \tag{10}$$

where δV_{sweep} is the volume change of the excluded volume sphere. The latter is related to the d-dimensional surface $S_d(2\sigma)$ of a sphere with radius 2σ through

$$\delta V_{\text{sweep}} = S_d(2\sigma)\frac{\delta\sigma}{2} = 2^{d-1}S_d(\sigma)\frac{\delta\sigma}{2}. \tag{11}$$

We sum over all particles in the system and obtain

$$\delta W_a = \sum_i \delta W_{\sigma\to\sigma+\delta\sigma} = \rho kTg(\sigma)2^{d-1}\delta V_p, \tag{12}$$

where δV_p is the change of the total volume occupied by the spheres and $\delta V_p/\delta V = \eta$ is the volume fraction.[14] We substitute Eq. (12) in Eq. (9) and obtain

$$-\rho kT = \rho kT2^{d-1}\eta g(\sigma) - P. \tag{13}$$

Hence, we obtain the equation of state

$$\frac{P}{\rho kT} = 1 + 2^{d-1}\eta g(\sigma). \tag{14}$$

To our knowledge, the simplest derivation of Eq. (14) involves the virial theorem,[11] and is more complicated and physically less transparent.[15] We stress that Eq. (14) is exact, but incomplete because $g(\sigma)$ is not known explicitly.

By comparing Eqs. (14) and (8) in one dimension, we find that the pair correlation function at contact takes the value[8,9]

$$g(\ell) = 1/(1-\eta). \tag{15}$$

It is straightforward to generalize Eqs. (12) and (14) to the polydisperse case with size distribution $f(\sigma)$ (see for example, Ref. 16, Appendix B). The result is

$$\frac{P}{\rho kT} - 1 = \eta\int d\sigma d\sigma' f(\sigma)f(\sigma')g(\sigma/2 + \sigma'/2)\frac{\sigma(\sigma+\sigma')^{d-1}}{\langle\sigma^d\rangle}, \tag{16}$$

where $\langle\sigma^d\rangle = \int\sigma^d f(\sigma)d\sigma$.

III. INCLUSION OF A KAC TAIL

It is instructive to consider a system of particles interacting with a Kac potential, because not only can the appropriate pressure be recovered, but also some light can be shed on the nature of the expansion processes underlying our arguments. We assume that, in addition to the usual hard-sphere term, particles interact with a very long range and weak pair potential so that the interaction potential is

$$\phi(r) = \begin{cases} \infty & \text{for } r<\sigma\equiv\ell \\ \gamma\exp(-r/r^*) & \text{for } r>\sigma, \end{cases} \tag{17}$$

where the range r^* is larger than any microscopic distance ($\rho r^*\gg 1$) and the strength γ is small.[17] This quantity can be positive (repulsive tail) or negative (attractive tail). It has been shown rigorously that the corresponding equation of state in one dimension is of the van der Waals form,[6]

$$P = \frac{\rho kT}{1-\eta} + \alpha\rho^2, \tag{18}$$

where $\alpha=\gamma r^*$. This result has been generalized to arbitrary dimensions,[7] in which case the correction to the hard-sphere pressure is $\alpha\rho^2$, with $\alpha = \int\phi(\mathbf{r})d^d\mathbf{r}/2$, where the integral runs outside the excluded volume sphere (that is, $r>\sigma$).

The result Eq. (18) holds irrespective of the precise form of $\phi(r)$ for $r>\sigma$,[2] as is clear from the following argument. We restrict ourselves to $d=1$, but the spatial dimension is largely immaterial. From $\delta W_{\text{total}} = \delta W_a + \delta W_b$, we have

$$(P-\rho kT)\delta L = \delta W_a, \tag{19}$$

and our goal is to calculate δW_a. In step (a) it is understood that the range of the potential r^* is expanded for fixed γ to remain proportional to the rod size ℓ: $\delta r^*/r^* = \delta\ell/\ell = \delta L/L$. A key point is that the $r>\ell$ part of the potential does not affect the relative positions of the particle from what they would have had as hard rods at the same density ρ.[7] This point follows from the fact that γ is very small.[17] The pair distribution function $g(r)$ is thus unaffected by the tail and $g(\sigma)$ is given by Eq. (15). When a given rod of size ℓ is expanded, the work necessary can be written as the sum of a kinetic contribution (one has to "push" the particles that are in direct contact with the particle of interest), and a (long-range) contribution arising from the tail of the potential,

$$\delta W_{\ell\to\ell+\delta\ell} = \rho_{\text{contact}}kT\delta\ell + \delta W_{\text{tail}} = \frac{\rho kT}{1-\eta}\delta\ell + \delta W_{\text{tail}}. \tag{20}$$

Because any particle experiences an average potential energy $2\gamma r^*\rho$, as follows from integrating Eq. (17), we have $\delta W_{\text{tail}} = \delta(2\gamma r^*\rho)$, where the variation is calculated at fixed values of γ and ρ. We sum over all particles and obtain

$$\delta W_a = \frac{\rho kT}{1-\eta}\eta\delta L + \frac{1}{2}N2\gamma\rho\delta r^*, \tag{21}$$

where the factor of 1/2 corrects for double counting. Because $\delta r^*/r^* = \delta L/L$, we arrive at

$$\delta W_a = \frac{\rho kT}{1-\eta}\eta\delta L + \underbrace{\gamma r^*}_{\equiv\alpha}\rho^2\delta L. \tag{22}$$

We substitute this result into Eq. (19) and obtain Eq. (18), a result otherwise difficult to derive.[6,7] As is clear, Eq. (18) indicates that a repulsive interaction (γ and $\alpha > 0$) leads to an enhanced pressure.

We emphasize that $\delta W_a \neq P\delta L_p$, where as before, $\delta L_p = \eta\delta L$ is the total length variation of the rods: expanding a given rod differs from moving a piston in that the piston has to be held fixed, while our move is for a given particle in the fluid that is therefore free to move. If we were to consider the particle to be expanded as fixed at a given location and with a slowly increasing size ($\ell \to \ell + \delta\ell$), the work required would reduce to $P\delta\ell$ because the particle would act as a piston. This work can again be expressed as the sum of a kinetic pressure term with the same value of the pair distribution at contact as given by Eq. (15), and the energy potential difference,

$$P\delta\ell = \rho_{\text{contact}} kT\delta\ell + \delta(N\gamma r^*\rho) = \rho\frac{1}{1-\eta}kT\delta\ell + \delta(N\gamma r^*\rho). \tag{23}$$

The difference with Eq. (21) is that now the range r^* is fixed, but the density varies according to $\delta\rho/\rho = -\delta L/L = \delta\ell/\ell$. Hence,

$$P\delta\ell = \frac{\rho}{1-\eta}kT\delta\ell + \gamma r^*\rho^2\delta\ell, \tag{24}$$

and we recover Eq. (18). In the absence of the Kac tail ($\gamma = 0$), fixing the expanded particle is unimportant, and the fact that $\delta W_a = P\delta L_p$ can be interpreted as a consequence of the hard potential (with interactions at contact only and a pressure that depends only—apart from factors of ρ and T—on the pair distribution function at contact).

IV. CONCLUDING REMARKS

We have proposed an exact derivation of the equation of state of hard-rod systems with and without a long-range pair potential. The scaling arguments can be easily extended to hard-core particles in higher dimensions, for example hard disks and hard spheres.

To our knowledge, pedagogical accounts avoiding mathematical complication on the present topics are scarce in the literature. We note however that a relatively simple approach which generalizes the original Bernoulli derivation of the ideal gas equation of state has been proposed.[18] In addition to being heuristic, this method cannot be applied if a Kac tail is present.

Finally, we note that our arguments are similar in spirit to scaled particle theory,[9–11,19] but are distinct. Scaled particle theory is based on the calculation of the reversible work needed to create a spherical cavity from which the centers of other spheres are excluded. This work is then related to the density of particles at contact with the cavity boundary, and can be worked out exactly in one dimension, because there are no curvature effects. The latter remark also explains why we were able to derive the pressure in closed form for $d = 1$.

ACKNOWLEDGMENT

We would like to thank Andres Santos for useful comments.

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[11] See for example, J.-P. Hansen and I. R. MacDonald, *Theory of Simple Liquids* (Academic Press, London, 2006) and J. L. Barrat and J.-P. Hansen, *Basic Concepts for Simple and Complex Fluids* (Cambridge U. P., Cambridge, 2003).

[12] To be more specific, we need to introduce reduced coordinates $\tilde{x}_i = x_i/L$ and reduced lengths $\tilde{\ell}_i = \ell_i/L$. The Hamiltonian expressed in terms of $\{\tilde{x}_i, \tilde{\ell}_i\}$ becomes L-independent so that the canonical partition function is $Z(T,L,N,\{\ell_i\}_{1\le i\le N}) = L^N\tilde{Z}(T,\{\tilde{\ell}_i\}_{1\le i\le N})$, For interactions other than hard core, this scaling relation for the partition function still holds, which immediately leads to Eq. (3).

[13] M. Bishop, “Virial coefficients for one dimensional hard rods,” Am. J. Phys. **51**, 1151–1152 (1983).

[14] The fundamental difference between $d = 1$ and higher space dimensions is that $P = \rho kTg(\sigma)$ in one dimension because the particle-particle pair distribution function at contact coincides with $g_{\text{pw}}(\sigma)$, the particle-wall distribution function at contact. For $d > 1$ $P = \rho kTg_{\text{pw}}(\sigma)$, which differs from $\rho kTg(\sigma)$.

[15] Another method, due to H. S. Green, may be found in T. L. Hill, *Statistical Mechanics* (Dover, New York, 1987), Chap. 6. This method relies on a general rescaling of particle sizes with system size, and is therefore reminiscent of the argument backing up Eq. (3), with the difference that in calculating the volume derivative of the partition function, the particle sizes are kept fixed.

[16] J. Zhang, R. Blaak, E. Trizac, J. A. Cuesta, and D. Frenkel, “Optimal packing of polydisperse hard sphere fluids,” J. Chem. Phys. **110**, 5318–5324 (1999).

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