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

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In this note, we propose a simple derivation of the one dimensional hard rod equation of state, with and without a Kac tail (appended long range and weak potential). The case of hard spheres in higher dimension is also addressed and it is shown there that our arguments—which avoid any mathematical complication—allow to recover the virial form of the equation of state in a direct way.

I. INTRODUCTION

The equation of state is a central object in the statistical mechanics description of matter. Bearing the signature of inter-particle interactions and being easily measured experimentally, it establishes a connection between microscopic and macroscopic features that long remained elusive. In particular, many efforts in the 19th century aimed at explaining the deviations from the ideal gas law. Progresses in the field have been hindered by the positivist storm of criticisms directed against kinetic theory and the associated atomistic viewpoint. Today, the machinery of statistical mechanics offers a consistent framework for those problems, with the pedagogical drawback that very few interacting systems have an equation of state that can be written in closed form.

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

\[
P = \frac{\rho kT}{1 - \eta},
\]

where \( kT \) is the thermal energy, \( \rho = N/L \) denotes the density, and \( \eta = \sum_i \ell_i/L \) is the line covering fraction (so that \( \eta/\rho \) is the mean rod length). In addition, several equilibrium and non-equilibrium quantities can be computed, and the model provides a reference system for perturbative treatments, one of which being addressed below, with inclusion of a so-called Kac pair potential of interaction between the particles.

In standard textbooks as well as in the original papers, the derivation of Eq. (1) is not straightforward, and it is our purpose here to propose an alternative concise argument relying on simple physical considerations rather than partition functions and mathematical computations. When transposed 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 density.

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 computing exactly the pressure, we consider several related “Gedankenexperiments”. We first make the remark that upon rescaling all lengths in the problem by a factor \( 1 + \epsilon \)

\[
\ell_i \rightarrow (1 + \epsilon)\ell_i \text{ for all } 1 \leq i \leq N, \quad L \rightarrow (1 + \epsilon)L,
\]

the reversible work \( \delta W_{\text{total}} \) associated with this process reduces to its ideal gas contribution since excluded volume is irrelevant in this transformation (it is of course essential to rescale the “box” length \( L \)) ; only the ideal entropy of mixing is affected in this simple “zoom”. We then have

\[
\delta W_{\text{total}} = -\rho kT \delta L,
\]

where \( \delta L = \epsilon L \) is the total length change. Equation (3) holds beyond hard body interactions and applies whenever the problem at hand is governed by a unique length scale. It would in particular hold for Lennard-Jones interactions. For \( \delta L > 0 \), the work \( \delta W_{\text{total}} \) is negative. If only the box length is expanded, the work \( \delta W_{\text{total}} \) received by the gas is obviously negative. The additional particle expansion considered here amounts to a positive contribution to \( \delta W_{\text{total}} \), which turns out to be smaller in absolute value than the former one. The resulting cost is negative, as the following discussion explicitly shows.
We now perform the expansion (2) in two steps and compute separately the corresponding reversible work required:

a) First, rod sizes are slowly and sequentially rescaled (i.e. one at a time):
\[ \ell_1 \rightarrow (1 + \epsilon_1)\ell_1, \, \ell_2 \rightarrow (1 + \epsilon_2)\ell_2, \ldots \]

b) Second, the confining box size is expanded
\[ L \rightarrow (1 + \epsilon) L. \]

It is essential to realize that 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 \( P \delta \ell_i = P \epsilon_i \ell_i \) (we comment further below this fundamental fact). Consequently, the work needed to perform step a) reads
\[ \delta W_a = \sum_{i=1}^{N} P \delta \ell_i = P \delta L_p, \tag{4} \]
where \( L_p \) is the total length occupied by the rods (here, \( \delta L_p = \eta \delta L \)).

For step b), the work reduces to
\[ \delta W_b = -P \delta L. \tag{5} \]

Summing both contributions, we have \( \delta W_{\text{total}} = \delta W_a + \delta W_b \) and gathering results, this implies
\[ -\rho kT \delta L = P \eta \delta L - P \delta L \implies P = \frac{\rho kT}{1 - \eta}, \tag{6} \]

which is the correct result. We stress that irrespective of the sign of the scaling parameter \( \epsilon \), the moves considered in steps a) and b) do not produce overlaps between particles nor between particles and confining boundaries, in the same way as a moving boundary like a piston does not lead to overlaps. We also note that from the form of the equation of state (6), all virial coefficients are unity. This can be checked by explicit calculations.[13]

Following the same line of reasoning, we investigate the problem of hard spheres in dimension \( d > 1 \). One still has
\[ \delta W_{\text{total}} = \delta W_a + \delta W_b \quad \text{with} \quad \delta W_{\text{total}} = -\rho kT \delta V, \tag{7} \]
\( V \) being now the volume of the system, and \( \delta W_b = -P \delta V \). However, \( \delta W_a \) is not as straightforwardly related to the pressure as in (4) and to obtain its expression, we introduce the pair correlation function \( g(r) \).[3, 11] For the sake of simplicity, we restrict to the monodisperse case where all particles have the same diameter \( \sigma \). The force per unit area felt by a given particle is of kinetic origin and reads \( \rho kT g(\sigma) \); remembering that a particle is surrounded by an excluded volume sphere of diameter \( 2\sigma \) where no other particle’s center of mass may be found, we can write the work needed to expand \( \sigma \) into \( \sigma + \delta \sigma \) as
\[ \delta W_{\sigma \rightarrow \sigma + \delta \sigma} = \rho kT g(\sigma) \delta V_{\text{sweep}}, \tag{8} \]
where \( \delta V_{\text{sweep}} \) is the volume change of the excluded volume sphere. The latter quantity is related to the \( d \)-dimensional surface \( S_d(2\sigma) \) of a sphere with radius \( 2\sigma \) through
\[ \delta V_{\text{sweep}} = S_d(2\sigma) \frac{\delta \sigma}{2} = 2^{d-1} S_d(\sigma) \frac{\delta \sigma}{2}. \tag{9} \]

Summing over all particles in the system, we get
\[ \delta W_a = \sum_i \delta W_{\sigma \rightarrow \sigma + \delta \sigma} = \rho kT g(\sigma) 2^{d-1} \delta V_p \tag{10} \]
where, keeping previous notation, \( \delta V_p \) is the change of the total volume occupied by the spheres and therefore \( \delta V_p / \delta V = \eta \), the volume fraction.[14] Returning to Eq.(7), we obtain
\[ -\rho kT = \rho kT 2^{d-1} \eta g(\sigma) - P, \tag{11} \]
and hence the equation of state
\[ \frac{P}{\rho kT} = 1 + 2^{d-1} \eta g(\sigma). \tag{12} \]

To our knowledge, the simplest derivation of this result involves the virial theorem[11] and turns out to be more complicated and physically less transparent.[15] As a by-product, comparing (12) and (6) in one dimension, we obtain that the pair correlation function at contact for hard rods takes the value
\[ g(\ell) = 1/(1 - \eta), \tag{13} \]
We also emphasize that it is straightforward to generalize (10) and (12) to the polydisperse case with size distribution $f(\sigma)$ (see e.g appendix B of Ref. [16]), with the result

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

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

### III. INCLUSION OF A KAC TAIL

It proves instructive to consider also the case of particles interacting with a so-called “Kac tail” since not only can the proper pressure be recovered, but also some light 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 reads

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

where $r^*$ is larger than any microscopic distance ($\rho r^* \gg 1$) and the amplitude $\gamma$ is small. This quantity can be positive (repulsive tail) or negative (attractive tail). It has been shown –with all mathematical $i$-s dotted– that the corresponding equation of state is of the van der Waals form and reads

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

where $\alpha = \gamma r^*$. This result has been generalized to an arbitrary space dimension in which case again, the correction to the hard sphere pressure is simply $\alpha \rho^2$, with now $\alpha = \int \phi(r) d^d r/2$, where the integral runs outside the excluded volume sphere (i.e. $r > \sigma$). Actually, the result holds irrespective of the precise form of the interaction potential, as is also clear from the following argument. We restrict to $d = 1$, but space dimension is largely immaterial. From $\delta W_{\text{total}} = \delta W_a + \delta W_b$, we have

$$(P - \rho kT) \delta L = \delta W_a,$$

and our objective is now to compute the latter term. In step a), it is understood that the range of the potential $r^*$ is expanded, at fixed amplitude $\gamma$, to remain proportional to the rod size $\ell$: $\delta r^*/r^* = \delta \ell/\ell = \delta L/L$. A key point in the analysis is that the tail $r > \ell$ of potential does not affect the relative positions of the particle from what they would have as hard rods at the same density $\rho$. This follows from the fact that the amplitude $\gamma$ should be taken extremely small. The pair distribution function $g(r)$ is thus unaffected by the tail and we have in particular the contact value (13). When a given rod of size $\ell$ 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 :

$$\delta W_a = \rho kT \frac{1}{1 - \eta} \delta L + \gamma r^* \rho \delta \ell.$$

Since any particle experiences an average potential energy $2\gamma r^* \rho$, as follows from integrating, we have $\delta W_{\text{tail}} = \delta (2\gamma r^* \rho)$ where the variation is computed at fixed amplitude and density. Summing over all particles, we obtain

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

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

$$\delta W_a = \frac{\rho kT}{1 - \eta} \eta \delta L + \gamma r^* \rho^2 \delta L.$$
It seems appropriate at this point to emphasize that $\delta W_a \neq P \delta L_p$ where as above, $\delta L_p = \eta \delta L$ 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 pertains to a given particle in the fluid, that is therefore free to move. If we would consider the particle expanded to be fixed at a given location, and with a slowly increasing size ($\ell \rightarrow \ell + \delta \ell$), the work required would reduce to $P \delta \ell$ since 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. (13), and an energy potential difference:

\begin{equation}
P \delta \ell = \rho_{\text{contact}} kT \delta \ell + \delta(N \gamma r^* \rho) \tag{21a}
\end{equation}

\begin{equation}
= \rho \frac{1}{1 - \eta} kT \delta \ell + \delta(N \gamma r^* \rho). \tag{21b}
\end{equation}

The difference with Eq. (19) is that now the range $r^*$ is fixed but the density varies according to $\delta \rho/\rho = -\delta L/L = \eta \delta \ell/L$.

Hence,

\begin{equation}
P \delta \ell = \rho \frac{1}{1 - \eta} kT \delta \ell + \gamma r^* \rho^2 \delta \ell, \tag{22}
\end{equation}

and we recover Eq. (19). In absence of the Kac tail ($\gamma = 0$), fixing or not the expanded particle is unimportant and the fact that we there have $\delta W_a = P \delta L_p$ can be viewed as a consequence of the hard potential used (with interactions at contact only and a pressure that only depends – apart from $\rho$ and $T$ – on the pair distribution function at contact)

IV. CONCLUDING REMARKS

We have proposed an exact derivation of the equation of state of certain simple liquids: hard rod systems with and without a long range pair potential of interaction (Kac tail). The argument – based on scaling considerations – can be easily extended to hard core particles in higher dimensions (hard discs, hard spheres…). The interest of the approach lies in its simplicity and it is our hope that the method put forward here is instructive and may be useful to illustrate an advanced undergraduate statistical mechanics course.

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 generalizing the original Bernouilli derivation of the ideal gas equation of state has been proposed.\[18\] In addition to being heuristic, this method could not be transposed to the case of Kac tails.

Finally, we note that our arguments bear some similarities with the scaled particle theory developed in the 1960s,\[8\][10][11][19] but are nevertheless distinct. Scaled particle theory is based on the computation of the reversible work needed to create a spherical cavity from which the centers of other spheres are excluded. This expression is then related to the density of particles at contact with the cavity boundary. This can be achieved exactly in one dimension, since there are then no curvature effects. The latter remark also explains why we have been able to derive the pressure in closed form for $d = 1$.

Acknowledgements

We would like to thank Andres Santos for useful comments.

[1] For a thorough historical overview, see S.G. Brush, “Development of the kinetic theory of gases”, Am. J. Phys. 29, 593-605 (1961).
[2] F.C. Andrews, Equilibrium Statistical Mechanics (John Wiley and Sons, 1975).
[3] D. Chandler, Introduction to Modern Statistical Mechanics, (Oxford University Press, 1987).
[4] L. Tonks, “The Complete Equation of State of One, Two and Three-Dimensional Gases of Hard Elastic Spheres”, Phys. Rev. 50, 955-963 (1936).
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To be more specific, this means that introducing reduced coordinates \( \bar{x}_i = x_i/L \) and reduced lengths \( \bar{\ell}_i = \ell_i/L \), the Hamiltonian expressed in terms of \( \{ \bar{x}_i, \bar{\ell}_i \} \) should be \( L \)-independent so that the canonical partition function reads

\[
Z(T, L, N, \{ \bar{\ell}_i \}_{1 \leq i \leq N}) = L^N \tilde{Z}(T, \{ \bar{\ell}_i \}_{1 \leq i \leq N}).
\]

(23)

For other interactions than hard core, the above scaling relation may still hold, which immediately leads to (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 one has \( P = \rho k T g(\sigma) \) in one dimension, since the particle-particle pair distribution function at contact then coincides with \( g_{pw}(\sigma) \), the particle-wall distribution function at contact. For \( d > 1 \), one has \( P = \rho k T g_{pw}(\sigma) \), which differs from \( \rho k T g_{p}(\sigma) \).

[15] Another method, due to H.S. Green, may be found in chapter 6 of T.L. Hill, Statistical Mechanics (Dover, 1987). It relies on a general rescaling of particle sizes with system size, and is therefore reminiscent of the technical argument backing up Eq. (2), with the difference that in computing the volume derivative of the partition function, 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).

[17] Formally, the limit \( r^* \to \infty, \gamma \to 0 \) with \( \gamma r^* \) fixed is required, and should be taken after the thermodynamic limit. [6, 7]

[18] F. Del Rio, E. Martina and M. Leiva, “Generalized Bernouilli construction – a heuristic approach to the equation of state”, Am. J. Phys. 42, 1083-1086 (1974).

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