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One-Dimensional Fluids with Positive Potentials

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Abstract We study a class of one-dimensional classical fluids with penetrable particles interacting through positive, purely repulsive, pair-potentials. Starting from some lower bounds to the total potential energy, we draw results on the thermodynamic limit of the given model.

Keywords Exact results · One-dimensional fluids · Thermodynamic limit

1 Introduction

Recently we found evidence that a non pairwise-additive interaction fluid model for penetrable classical particles living in one-dimension does not admit a well defined thermodynamics [1], but can only exist in a zero pressure state.

We know that physical pairwise-additive models could also have the same thermodynamic singularity. Whereas the Ruelle stability principle [2] tells us only that a fluid of N particles with a total potential energy, V_N, bounded from below, $V_N > NB$ with B a constant, cannot have a divergent pressure, it does not tell us whether it can only have a zero pressure in the thermodynamic limit. This happens for example for models with penetrable particles interacting with a positive, purely repulsive, long-range pair-potential v.

We will consider some lower bounds to the total potential energy V_N which will allow us to prove some important results regarding the thermodynamic limit of the underlying one-dimensional fluid model.

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2 The Problem

The grand canonical partition function of a system of particles in the segment $[0, L]$ whose positions are labeled by x_i with $i = 1, 2, \ldots, N$, in thermal equilibrium at a reduced temperature θ, is given by

$$\Omega = \sum_{N=0}^{\infty} \frac{z^N}{N!} \int_0^L dx_N \cdots \int_0^L dx_1\, e^{-\frac{V_N(x_1,\ldots,x_N)}{\theta}}, \tag{2.1}$$

where $z > 0$ is the activity. The total potential energy of the system is

$$\begin{aligned} V_N(x_1, \ldots, x_N) &= \sum_{i<j} v(|x_i - x_j|) \\ &= \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} v(|x_i - x_j|), \end{aligned} \tag{2.2}$$

where $v(x)$ is the pair-potential. We will assume that $v(x) \le v(0) = v_0 < \infty$ for all x, *i.e. penetrable* particles. For $v = 0$ we have the ideal gas (id).

Since $\Omega > 1$ we must have for the fluid pressure P

$$\frac{P}{\theta} = \lim_{L\to\infty} \frac{\ln \Omega}{L} > 0, \tag{2.3}$$

so the pressure cannot be negative. In addition we will assume that $v(x)$ is a *positive* function, $v(x) > 0$ for all x, then

$$\begin{aligned} \frac{P}{\theta} &= \lim_{L\to\infty} \frac{\ln \Omega}{L} \\ &< \lim_{L\to\infty} \frac{\ln\left[\sum_{N=0}^{\infty} \frac{(zL)^N}{N!}\right]}{L} = z. \end{aligned} \tag{2.4}$$

So $0 < P < \theta z$.

Let us furthermore assume that $v(x)$ has tails decaying to zero at large x and such that, for all x in $[0, L]$,

$$v(x) > v(L), \tag{2.5}$$

with

$$\lim_{L\to\infty} v(L) = 0. \tag{2.6}$$

Then we find

$$\Omega < \sum_{N=0}^{\infty} \frac{(zL)^N}{N!} e^{-\frac{v(L)N(N-1)}{2\theta}}, \tag{2.7}$$

and for the pressure,

$$\begin{aligned}\frac{P}{\theta} &= \lim_{L\to\infty}\frac{\ln\Omega}{L}\\ &< \lim_{L\to\infty}\frac{\ln\left[\sum_{N=0}^{\infty}\frac{(zL)^N}{N!}e^{-\frac{v(L)N(N-1)}{2\theta}}\right]}{L}\\ &= \lim_{L\to\infty}\frac{\ln\left[\int_0^\infty dy\,\frac{(zL)^{y/\sqrt{v(L)}}}{[y/\sqrt{v(L)}]!}e^{-\frac{y(y-\sqrt{v(L)})}{2\theta}}\right]-\ln[\sqrt{v(L)}]}{L},\end{aligned} \tag{2.8}$$

where we introduced the new continuous variable $y = N\sqrt{v(L)}$ to transform the series into an integral over y. Clearly if we had $\lim_{L\to\infty} v(L) = v_\infty$ with $v_\infty > 0$ a constant, we could immediately conclude that the limit in Eq. (2.8) is zero (see Eq. (5.5)) and the fluid has a singular thermodynamic limit. Since the pair-potential is defined always up to an additive constant, in this case, in order to find a reasonable result, one needs to properly scale the chemical potential as follows: $\ln(z) \to \ln(z) + v_\infty(N-1)/2\theta$.

Let us now introduce the Inverse Power Law Model (IPLM-α), $v(x) = v_0/[(|x|/\sigma)^\alpha + 1]$, with v_0, σ, and α three positive constants, and the Generalized Exponential Model (GEM-α), $v(x) = v_0 e^{-\gamma(|x|/\sigma)^\alpha}$, with γ a fourth positive constant. For the IPLM-α with $\alpha < 1$ the limit on the right hand side of Eq. (2.8) is equal to zero (see Eq. (5.15)) and the fluid can only exist in its zero pressure state. For $1 \le \alpha < 2$ it is non-zero smaller than z. For $\alpha \ge 2$ it is equal to z (see Eq. (5.14)), *i.e.* it has the ideal gas behavior. For the GEM-α the limit is also always equal to z.

On the other hand we can obtain a more stringent upper bound to the pressure observing that for models with a pair-potential with monotonically decaying tails, *i.e.* with $v'(x) < 0$ for all x or purely *repulsive*, like the ones we just introduced, the configuration of minimum potential energy is approximately the one with all particles equally spaced on the segment, so

$$\begin{aligned}\min(V_N) &= [1 + a(\alpha, N, L)]\sum_{i<j} v\left[\frac{(j-i)L}{N-1}\right]\\ &= [1 + a(\alpha, N, L)](N-1)\sum_{k=1}^{N} v\left[\frac{kL}{N-1}\right]\\ &> [1 + a(\alpha, N, L)](N-1)v\left(\frac{L}{N-1}\right).\end{aligned} \tag{2.9}$$

For example we find, in Eq. (2.9), $a(\alpha, 3, L) = 0$ and for $N > 3$ we generally have $a < 0$. Moreover,

$$\lim_{\alpha\to\infty} a = \lim_{L\to\infty} a = 0, \tag{2.10}$$

$$\lim_{\alpha\to 0} a = \lim_{L\to 0} a = 0. \tag{2.11}$$

Clearly $\lim_{N\to 0} a = 0$ and we must also have

$$0 < \lim_{N\to\infty} [1 + a(\alpha, N, L)] \le 1. \tag{2.12}$$

So $a(\alpha, N, L)$ remains finite for all α, L, and N since it must be a continuous function.

Then we will have

$$\frac{P}{\theta} < \lim_{L\to\infty} \frac{\ln\left[\sum_{N=0}^{\infty} \frac{(zL)^N}{N!} e^{-\frac{[1+a]\sum_{i<j} v\left[\frac{(j-i)L}{N-1}\right]}{\theta}}\right]}{L}. \tag{2.13}$$

We want to study the limit on the right hand side

$$\mathcal{L} = \lim_{L\to\infty} \frac{\ln\left[\sum_{N=0}^{\infty} \frac{(zL)^N}{N!} e^{-\frac{[1+a]\sum_{i<j} v\left[\frac{(j-i)L}{N-1}\right]}{\theta}}\right]}{L}. \tag{2.14}$$

Now we observe that for finite L,

$$\begin{aligned}\lim_{N\to\infty} \frac{L}{N^2} \sum_{i<j} v\left[\frac{(j-i)L}{(N-1)}\right] &= \int_0^L dx\, v(x)\\ &= b(\alpha, L),\end{aligned} \tag{2.15}$$

where $b(\alpha, L)$ diverges at large L for the IPLM-α with $\alpha \le 1$. Then the limit of Eq. (2.14) can be easily found for the IPLM-α with $\alpha \le 1$, as

$$\mathcal{L} = \lim_{L\to\infty} \frac{\ln\left[\sum_{N=0}^{\infty} \frac{(zL)^N}{N!} e^{-\frac{[1+a]bL^{-1}N^2}{\theta}}\right]}{L} = 0. \tag{2.16}$$

So we conclude that also the IPLM-α with $\alpha = 1$ does not have a well defined thermodynamic limit. A pair-potential such that $\lim_{L\to\infty} b$ is a finite constant, is said to be *short range*.

Note that the GEM-α for $\alpha = 1$ reduces to the Exponential Model (EM), for $\alpha = 2$ to the Gaussian Core Model (GCM), and taking the $\alpha \to \infty$ limit of either the GEM-α or the IPLM-α,

$$\lim_{\alpha\to\infty} v(x) = \begin{cases} v_0 & |x| < \sigma \\ 0 & |x| > \sigma \end{cases} \tag{2.17}$$

we find the Penetrable Rods Model (PRM). For the PRM the thermodynamics is well defined as follows from the analytic solution of the Tonks gas [3] for the Hard Rods Model (HRM). In fact we must have

$$\Omega_{\mathrm{HRM}} < \Omega_{\mathrm{PRM}} < \Omega_{\mathrm{id}} = e^{zL}. \tag{2.18}$$

According to our analysis, the IPLM-α and the GEM-α are non-singular for $\alpha \to \infty$ and the IPLM-α is singular for $\alpha \le 1$.

Moreover as already noticed in Ref. [1] the GEM-α with $\gamma \propto L^{-\alpha}$ are singular as immediately follows from Eq. (2.8) and Eq. (5.5).

3 External Potential

In order to regularize the models introduced in the previous section, the IPLM-α for $\alpha \le 1$, which have a long-range pair-potential, it is necessary to introduce a confining negative external potential which will prevent the particles to "escape" to infinity on the line.

Then we will have

$$V_N(x_1,\ldots,x_N)=\sum_{i<j}v(|x_i-x_j|)+N\sum_i\phi(x_i) \tag{3.1}$$

with ϕ the external potential such that $\phi(x)<-v_0/2$ for all x in $[0,L]$. So that we must now have $P/\theta>ze^{-v_0/2\theta}$.

4 Thermodynamic Regularity

In this section we want to discuss about the thermodynamic regularity of the IPLM-α for $\alpha>1$, which are *short-range*. We know that $P<\theta z$. So we should look for a non-zero lower bound to the pressure. We also know that the IPLM-∞ is equivalent to the PRM which is regular. So we can assume the IPLM-α to remain regular in a neighborhood of $\alpha\to\infty$. The property that $v(x)\le v_0$ implies $V_N\le N(N-1)v_0/2$ which in turn implies $P\ge 0$ which is not enough to say that P must be non-zero.

Even if it looks plausible to assume that short-range models should admit a regular thermodynamic limit we are unable to find a general principle rigorously proving such an assumption.

5 A Particular Non Pairwise-Additive Model

In Ref. [1] we studied the fluid model with

$$V_N=\sum_{i<j}w(x_i,x_j), \tag{5.1}$$

$$w(x_i,x_j)=v_0\prod_{k=i}^{j-1}A(|x_k-x_{k+1}|), \tag{5.2}$$

$$A(x)=v(x)/v_0, \tag{5.3}$$

where $x_1\le x_2\le\ldots\le x_N$. Proceeding as in Sect. 2 we may assume that for equally spaced particles

$$V_N\gtrsim \text{constant}\,(N-1)\sum_{k=1}^{N}\left[A\left(\frac{L}{N-1}\right)\right]^k,$$

so that from the properties of the geometric series in the large N limit

$$\sum_{k=1}^{N}\left[A\left(\frac{L}{N-1}\right)\right]^k\sim\frac{1-[A(L/N)]^N}{1-A(L/N)}, \tag{5.4}$$

and choosing for v the GEM-α, this behaves as N for $\alpha>1$ as $(1-e^{-L})N/L$ for $\alpha=1$, and as $(N/L)^\alpha$ for $\alpha<1$. So from the limit in Eq. (5.5) we conclude immediately that the model is thermodynamically singular for $\alpha>1$ with a zero pressure, in agreement with the results of Ref. [1]. Nothing can be said for $\alpha\le 1$. The case $\alpha=1$ reduces to the physical pairwise additive model.

6 Ensemble Equivalence

In this section we discuss the equivalence of the three thermodynamic ensembles of statistical physics, *i.e.* the grand canonical, the canonical, and the microcanonical. The argument for the equivalence can be found in any textbook on statistical physics, as for example in the Course of Theoretical Physics of Landau and Lifshitz [4]. We briefly retrace the argument below and in the next two subsections.

We divide a closed system, after a period of time long enough respect to its relaxation time, in many microscopic parts and consider one in particular. We call $\rho(q, p) = w(E(q, p))$ the distribution function for such part, where $q = (x_1, x_2, \ldots)$ are the particles coordinates and $p = (p_1, p_2, \ldots)$ their momenta. In order to obtain the probability $W(E)dE$ that the subsystem has an energy between E and $E + dE$ we must multiply $w(E)$ by the number of states with energies in this interval. We call $\Gamma(E)$ the number of states with energies less or equal to E. Then the required number of states between E and $E + dE$ can be written $(d\Gamma(E)/dE)dE \propto dqdp$ and the energy probability distribution is $W(E) = (d\Gamma(E)/dE)w(E)$. With the normalization condition $\int W(E)dE = 1$. The function $W(E)$ has a well defined maximum in $E = \bar{E}$ and a typical width ΔE such that $W(\bar{E})\Delta E = 1$ or $w(\bar{E})\Delta\Gamma = 1$, where $\Delta\Gamma = (d\Gamma(\bar{E})/dE)\Delta E$ is the number of states corresponding to the energy interval ΔE. This is also called the *statistical weight* of the macroscopic state of the subsystem, and its logarithm $S = \ln \Delta\Gamma$, is called *entropy* of the subsystem. The *microcanonical* distribution function for the closed system is $dw \propto \delta(E - E_0) \prod_i (d\Gamma_i/dE_i)dE_i \propto \delta(E - E_0)e^S \prod_i dE_i$, where E_0 is the constant energy of the closed system and we used the fact that the various subsystems are statistically independent so that $\Delta\Gamma = \prod_i \Delta\Gamma_i$ and $S = \sum_i S_i$. We know that the most probable values of the energies E_i are the mean values $\bar{E}_i$. This means that $S(E_1, E_2, \ldots)$ must have its maximum when $E_i = \bar{E}_i$. But the $\bar{E}_i$ are the energy values of the subsystems which corresponds to the complete statistical equilibrium of the system. So we reach the important conclusion that the entropy of the closed system, in a state of complete statistical equilibrium, has its maximum value, for a given energy E_0 of the closed system.

6.1 Canonical vs Microcanonical

Let us now come back to the problem of finding the distribution function of the subsystem, *i.e.* of any small macroscopic part of the big closed system. We then apply the microcanonical distribution to the whole system, $dw \propto \delta(E + E' - E_0)d\Gamma d\Gamma'$, where $E, d\Gamma$ and $E', d\Gamma'$ refer to the subsystem and to the *rest* respectively, and $E_0 = E + E'$. Our aim is to find the probability $w(q, p)$ of a state of the system in such way for the subsystem be in a well defined state (with energy $E(q, p)$), *i.e.* in a well defined macroscopic state. We then choose $d\Gamma = 1$, pose $E = E(q, p)$ and integrate respect to Γ', $w(q, p) \propto \int \delta(E(q, p) + E' - E_0)d\Gamma' \propto (e^{S'})_{E'=E_0-E(q,p)}$. We use the fact that since the subsystem is small then its energy $E(q, p)$ will be small respect to E_0, $S'(E_0 - E(q, p)) \approx S'(E_0) - E(q, p)dS'(E_0)/dE_0$. The derivative of the entropy respect to the energy is just $\beta = 1/\theta$ where θ is the reduced temperature of the closed system which corresponds with that of the subsystem in equilibrium. Then we find $w(q, p) \propto e^{-\beta E(q,p)}$ which is the well known *canonical* distribution.

6.2 Grand Canonical vs Canonical

We want now generalize the canonical distribution to a subsystem with a variable number of particles. Now the distribution function will depend both on the energy and on the number of particles N. The energies $E(q, p, N)$ will be different for different values of N. The probability that the subsystem contains N particles and be in the state (q, p) will be $w(q, p, N) \propto e^{S'(E_0-E(q,p,N),N_0-N)}$. Let then expand S' in powers of $E(q, p, N)$ and N keeping just the linear terms, so that $S'(E_0 - E(q, p, N), N_0 - N) \approx S'(E_0, N_0) - \beta E(q, p, N) + \beta\mu N$, where the chemical potential μ and the temperature of the subsystem and the rest are the same, since we require equilibrium. So we obtain for the distribution function $w(q, p, N) \propto e^{\beta(\mu N-E(q,p,N))}$. We can define the *activity* as $z = e^{\beta\mu}$. This is the *grand canonical* distribution we chose to use throughout our discussion.

6.3 On the Ensemble Equivalence in our Models

The ensemble equivalence may fail when approaching a phase transition when the fluctuations become so large that the linear approximation used above fails [5,6]. This is not the case for the models studied in the present work which do not admit a gas-liquid phase transition since the pair-potential is lacking a negative part (even if we cannot exclude a liquid-solid transition). All three distribution described above, the microcanonical, the canonical, and the grand canonical are in principle suitable for determining the thermodynamic properties of our models. The only difference from this point of view lies in the degree of mathematical convenience. In proactive the microcanonical distribution is the least convenient and is never used for this purpose. The grand canonical distribution is usually the most convenient. For example the Ruelle stability principle [2] holds only in this ensemble. This justifies our choice throughout the work.

7 Conclusions

For a one-dimensional fluid model we consider some lower bounds to the total potential energy V_N which allow us to prove some results regarding its thermodynamic limit. In particular we study fluids of penetrable particles interacting with a positive purely repulsive pair-potential with tails decaying to zero at infinite separations. We study two kinds of models: The IPLM-α and the GEM-α. For the long-range models, *i.e.* the IPLM-α for $\alpha \le 1$, the fluid can only exist in its zero pressure state. For the short-range models we are not able to draw any conclusion.

We find good evidence that a particular non pairwise-additive model already introduced in a recent previous work [1] is thermodynamically singular.

Our results could give some insights to prove the thermodynamic limit of more complex fluids such as the ones described in [7–11].

Appendix 1: Some Limits

We have

$$\lim_{L\to\infty} \frac{\ln\left[\sum_{N=0}^{\infty} \frac{(zL)^N}{N!} e^{-N^{1+\epsilon}}\right]}{L} = \begin{cases} z & \epsilon \le -1 \\ l & -1 < \epsilon < 0 \\ z/e & \epsilon = 0 \\ 0 & \epsilon > 0 \end{cases} \tag{5.5}$$

with $z/e < l < z$. For example to prove the last case $\epsilon > 0$ we can observe that

$$\frac{(zL)^N}{N!}e^{-N^{1+\epsilon}} = \frac{(zL/e^d)^N}{N!}e^{-N(N^\epsilon - d)} \tag{5.6}$$

$$< \frac{(zL/e^d)^N}{N!}, \quad \text{for} \quad N > d^{1/\epsilon}. \tag{5.7}$$

Then for any finite $d > 0$ we will find

$$0 < \lim_{L\to\infty} \frac{\ln\left[\sum_{N=0}^{\infty}\frac{(zL)^N}{N!}e^{-N^{1+\epsilon}}\right]}{L} < \frac{z}{e^d}. \tag{5.8}$$

Since d can be chosen very large but finite, then the limit of Eq. (5.5) must be zero.

Also

$$\lim_{L\to\infty} \frac{\ln\left[\sum_{N=0}^{\infty}\frac{(zL)^N}{N!}e^{-N/L}\right]}{L} = \lim_{L\to\infty} ze^{-1/L} = z. \tag{5.9}$$

And

$$\sum_{N=0}^{\infty}\frac{(zL)^N}{N!}e^{-(N/L)^2} \tag{5.10}$$

$$= \sum_{N=0}^{\infty}\frac{(zL)^N}{N!}\sum_{k=0}^{\infty}(-)^k\frac{(N/L)^{2k}}{k!} \tag{5.11}$$

$$= \sum_{k=0}^{\infty}(-)^k\frac{(z^2)^k}{k!}\sum_{N=0}^{\infty}\frac{(zL)^{N-2k}}{N!/N^{2k}} \xrightarrow{L\gg\sigma} \tag{5.12}$$

$$\sum_{k=0}^{\infty}(-)^k\frac{(z^2)^k}{k!}\sum_{N=2k}^{\infty}\frac{(zL)^{N-2k}}{N!/N^{2k}} = e^{-z^2}e^{zL}, \tag{5.13}$$

so

$$\lim_{L\to\infty} \frac{\ln\left[\sum_{N=0}^{\infty}\frac{(zL)^N}{N!}e^{-(N/L)^2}\right]}{L} = \lim_{L\to\infty} z - z^2/L = z. \tag{5.14}$$

Proceeding as above we can also prove that for the IPLM-α with $\alpha > 2$ and all the GEM-α we must have $P < \theta z$.

Moreover we have

$$0 < \frac{\ln\left[\sum_{N=0}^{\infty}\frac{(zL)^N}{N!}e^{-v(L)N^2}\right]}{L}$$

$$< \frac{\ln\left[\sum_{N=0}^{\infty}(zL)^N e^{-v(L)N^2}\right]}{L}$$

$$= \frac{\ln\left[e^{[\ln(zL)]^2/4v(L)}\sum_{N=0}^{\infty} < e^{-v(L)[N-\ln(zL)/2v(L)]^2}\right]}{L}$$

$$
\begin{aligned}
&< \frac{\ln\left[e^{[\ln(zL)]^2/4v(L)} \sum_{N=0}^{\infty} e^{-v(L)N^2}\right]}{L} \\
&= \frac{[\ln(zL)]^2}{4v(L)L} + \frac{\ln\left[\int_0^{\infty} dy\, e^{-y^2}\right]}{L} - \frac{\ln[v(L)]}{2L}.
\end{aligned} \tag{5.15}
$$

Then, since for the IPLM-α with $\alpha < 1$ the limit of the last expression is zero, its pressure must be zero as mentioned in the main text.

References

1. Fantoni, R.: Exact results for one dimensional fluids through functional integration. J. Stat. Phys. **163**, 1247–1267 (2016)
2. Ruelle, D.: Statistical Mechanics: Rigorous Results. Benjamin, London (1969)
3. Tonks, L.: The complete equation of state of one, two and three-dimensional gases of hard elastic spheres. Phys. Rev. **50**, 955 (1936)
4. Landau, L.D., Lifshitz, E.M.: Statistical Physics. In: Lifshitz, E.M., Pitaevskii, L.P. (eds.) Course of Theoretical Physics, vol. 5. Butterworth-Heinemann, Oxford (1980). translated from the Russian by J. B. Sykes and M. J. Kearsley
5. Touchette, H.: Equivalence and nonequivalence of ensembles: thermodynamic, macrostate, and measure levels. J. Stat. Phys. **159**, 987–1016 (2015)
6. Costeniuc, M., Ellis, H.T.R.S., Turkington, B.: Generalized canonical ensembles and ensemble equivalence. Phys. Rev. E **73**, 026105 (2006)
7. Fantoni, R.: A cluster theory for a Janus fluid. Eur. Phys. J. B. **85**, 108 (2012)
8. Fantoni, R., Malijevský, A., Santos, A., Giacometti, A.: Phase diagram of the penetrable square well-model. Europhys. Lett. **93**, 26002 (2011)
9. Gazzillo, D., Fantoni, R., Giacometti, A.: Fluids of spherical molecules with dipolarlike nonuniform adhesion: an analytically solvable anisotropic model. Phys. Rev. E. **78**, 021201 (2008)
10. Maestre, M.A.G., Fantoni, R., Giacometti, A., Santos, A.: Janus fluid with fixed patch orientations: theory and simulations. J. Chem. Phys. **138**, 094904 (2013)
11. Fantoni, R., Giacometti, A., Maestre, M.A.G., Santos, A.: Phase diagrams of Janus fluids with up-down constrained orientations. J. Chem. Phys. **139**, 174902 (2013)