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On Discontinuity of the Pressure

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Abstract. A class of one-dimensional classical lattice gas models with translationally invariant, stable and strongly tempered many-body interactions, is constructed for which the limiting thermodynamic pressure is a discontinuous function of the density (at fixed temperature). This demonstrates that an apparently "mild" restriction on the potential ("supersummability") employed by Griffiths and Ruelle in proving the continuity of the pressure in lattice systems, plays, in fact, a crucial role.

I. Introduction

Following the earliest result by Ruelle [1] (for a classical gas with bounded, strongly tempered, and stable pair interactions) the question of proving the continuity of the pressure p, as a function of the density ϱ, at fixed temperature T, has been considered by a number of authors [2–5]. Of course, such continuity has, so far, always been observed experimentally: nevertheless, it is not demanded by thermodynamics and, indeed, the existing proofs require certain restrictions on the potentials over and above those needed for the existence of a proper thermodynamic limit. The strongest result to date was obtained recently by Griffiths and Ruelle [5], and concerns classical and quantum lattice gases. Under restrictions to be mentioned shortly, they established the *strict convexity* of the limiting thermodynamic potential p, as a function of any parameter entering the Hamiltonian linearly. The chemical potential μ, is such a parameter; the graph of p versus μ thus has no straight segments; hence the graph of $\varrho = (\partial p/\partial \mu)$ versus μ has no level (constant) sections; finally, therefore p is a continuous function of ϱ.

To state the conditions employed by Griffiths and Ruelle let $U(X)$ denote the (real) total potential energy of a set X of $N(X)$ (distinct) occupied lattice sites $\boldsymbol{r}_1, \ldots, \boldsymbol{r}_N \in X$. (Two particles may not occupy the same site.) We will eventually consider a one-dimensional lattice, for which $\boldsymbol{r} \equiv r = na$ $(n = 0, \pm 1, \pm 2, \ldots)$; for the present, however, the lattice $\mathscr{L}$ need not be specified beyond its translational invariance and local finiteness. For the existence of the thermodynamic limit the following conditions are known to be sufficient [1, 6, 7]:

T *Translational Invariance*

$$U(X + \boldsymbol{r}_0) = U(X), \quad \textit{all } \boldsymbol{r}_0 \in \mathscr{L}, \tag{1.1}$$

which is a natural requirement;

A *Stability*

$$U(X) \geqq -w_A N(X), \quad \textit{for all } X \ (w_A < \infty), \tag{1.2}$$

which restricts the attractive (negative) parts of the potential; and

B* *Strong Tempering*

$$U(X \cup X') \leqq U(X) + U(X') \quad \textit{whenever} \quad R(X, X') \geqq R_0 < \infty, \tag{1.3}$$

where $R(X, X') = \min|\boldsymbol{r} - \boldsymbol{r}'|$, denotes the shortest distance between lattice sites $\boldsymbol{r} \in X$ and $\boldsymbol{r}' \in X'$. This tempering condition restricts the total repulsive (positive) interaction between separated groups of particles; less restrictive, weak tempering, conditions also suffice [6, 7].

In terms of the many-body potentials $\Phi(Y)$, with

$$\Phi(Y) \equiv \Phi_l(\boldsymbol{r}_1 \ldots \boldsymbol{r}_l) \quad \textit{when} \quad Y = \{\boldsymbol{r}_1, \ldots \boldsymbol{r}_l\}, \quad \textit{and} \quad \Phi_1(\boldsymbol{r}) = \mu, \tag{1.4}$$

we have

$$U(X) = \sum_{Y \subset X} \Phi(Y). \tag{1.5}$$

It is then easy to see [6, 7], that the condition

$\boldsymbol{A}_0$ *Summability*

$$\|\Phi\| = \sum_{Y \ni \boldsymbol{r}_0} |\Phi(Y)|/N(Y) < +\infty, \tag{1.6}$$

implies stability. (The sum without the modulus signs merely represents the energy per site of a fully occupied lattice.) On the other hand, Griffiths and Ruelle imposed, what they termed, the "mild" additional condition

$\boldsymbol{A}_0^+$ *Supersummability*

$$\|\Phi\|^+ = \sum_{Y \ni \boldsymbol{r}_0} |\Phi(Y)| < +\infty. \tag{1.7}$$

Evidently, this condition represents a stronger restriction on the high order many-body interactions than does simple summability. (The sum in (1.7) represents a bound on the total interaction of *one* particle with all the others.)

The purpose of this note is to demonstrate that, despite its apparent "mildness", this supersummability condition, $\boldsymbol{A}_0^+$, plays a crucial role in the Griffiths-Ruelle proof and, thence, in the continuity of the pressure. This will be achieved by constructing a class of exactly soluble one-dimensional lattice gas models (generalizing somewhat a type previously studied [8–10]) in which the potentials satisfy the conditions ***T***, ***B****, and $\boldsymbol{A}_0$ but do *not* satisfy $\boldsymbol{A}_0^+$. For these models the pressure exhibits a dis-

continuity as a function of the density at finite density for a range of temperatures, even when the sum defining $\|\Phi\|^+$ diverges only logarithmically.

II. Cluster Interaction Models

In Ref. [8] a class of exactly soluble one-dimensional continuum classical gas models was defined in which many-body potentials were introduced through a clustering mechanism. In particular, if two adjacent particles, located at r_i and r_{i+1}, were closer than the *clustering distance* c, that is $|r_{i+1} - r_i| < c$, then the two particle belonged to the same cluster. Conversely, particles in the same cluster of l particles experienced a supplementary many-body potential depending on l. For suitable potentials such a gas exhibits a wide variety of phase transitions, [8–10]. As pointed out in Ref. [8], one can extend the definition of a cluster by also requiring that two adjacent particles belonging to the same cluster should not be closer together than some *lower clustering distance* $c' < c$. All these models are easily adapted to a lattice rather than a continuum. It then turns out, as will be shown, that the introduction of a (nontrivial) lower clustering distance is sufficient to generate discontinuities in the (p, ϱ) isotherms.

Without further ado, the lattice gas models to be considered are defined on the linear lattice

$$r = na \quad \textit{with} \quad n = 0, \pm 1, \pm 2, \ldots , \tag{2.1}$$

and have a pair interaction potential

$$\Phi_2(r_1, r_2) = \varphi_2(|r_2 - r_1|) \tag{2.2}$$

with

$$\varphi_2(0) = +\infty, \quad \varphi_2(a) = -v, \quad \textit{and} \quad \varphi_2(r) = 0, \quad \textit{for} \quad r > a\,. \tag{2.3}$$

The clustering distance is taken as $c = 3a$ and the lower clustering distance as $c' = 2a$; thus, in an l-cluster the particle spacing is fixed at $\Delta r = 2a$. The l-body interaction for $l \geqq 3$ is thence defined by

$$\begin{aligned} \Phi_l(r_1, \ldots, r_l) &= -v_l \quad \textit{provided} \quad r_{j+1} - r_j = 2a \quad \textit{for} \quad j = 1, 2, \ldots l-1\,, \\ &= 0, \qquad \textit{otherwise}\,. \end{aligned} \tag{2.4}$$

These potentials are clearly translationally invariant and satisfy the strong tempering condition $\boldsymbol{B}^*$ for any $R_0 > c$. The norms entering the conditions $\boldsymbol{A}_0$ and $\boldsymbol{A}_0^+$ are easily seen to be

$$\|\Phi\| = |\mu| + |v| + \sum_{l=3}^{\infty} |v_l|\,, \tag{2.5}$$

and

$$\|\Phi\|^+ = |\mu| + 2|v| + \sum_{l=3}^{\infty} l|v_l| . \tag{2.6}$$

To ensure stability we will choose the v_l so that

$$\|\Phi\| < +\infty . \tag{2.7}$$

The total energy of an isolated l-cluster can now be written as

$$U^{(l)} = (l-1)\,\varphi_\infty + W(l) , \tag{2.8}$$

where the "bulk" contribution per particle is

$$-\varphi_\infty = W(2) = \sum_{k=3}^{\infty} v_k , \tag{2.9}$$

whence the effective "surface" energy is given by

$$W(l) = \sum_{k=3}^{\infty} \min\{k-2, l-1\} v_k , \qquad W(1) = 0 , \tag{2.10}$$

the sums being convergent by (2.7). This relation can be inverted to yield

$$v_l = -W(l) + 2W(l-1) - W(l-2) \tag{2.11}$$

for $l \geqq 3$, and

$$V_l^+ = \sum_{k=3}^{l} k v_k = (l+1)\,W(l-1) - lW(l) . \tag{2.12}$$

From these expressions one finds that the surface energy $W(l)$ satisfies

$$W(l)/l \to 0, \quad as \quad l \to \infty . \tag{2.13}$$

On the other hand, to achieve a pressure discontinuity, we will require $W(l) \to \infty$. To see the significance of this, suppose, for simplicity, that

$$v_k \geqq 0 \quad all \quad k > 2 . \tag{2.14}$$

Then from (2.10) we obtain

$$V_l^+ - 2W(2) \leqq W(l) \leqq V_\infty^+ \leqq +\infty . \tag{2.15}$$

It follows that $W(l) \to \infty$, as $l \to \infty$, if and only if $V_\infty^+ = +\infty$, which by (2.12) and (2.6) is equivalent to the violation of the supersummability condition A_0^+. Finally, note that through (2.3), (2.9), and (2.11), the model is fully defined by specifying v and the function $W(l)$ for $l \geqq 2$.

III. Analysis of the Models

The grand partition function for a finite segment Λ of the lattice, of length $L = N(\Lambda)$ sites, at inverse temperature

$$\beta = 1/k_B T, \tag{3.1}$$

and activity

$$z = e^{\beta\mu} = \exp(-\beta\Phi_1), \tag{3.2}$$

is defined by

$$\Xi_L(z) = \sum_{X \subset \Lambda} \exp[-\beta U(X)], \tag{3.3}$$

and, by (2.7) and (2.5), has the bound

$$\Xi_L(z) \leqq 2^L \exp(L\beta \|\Phi\|). \tag{3.4}$$

The limiting thermodynamic pressure $p(z)$ is defined through

$$\beta p(z) a = \lim_{L \to \infty} (1/L) \ln \Xi_L(z), \tag{3.5}$$

which limit exists by previous results [1, 6, 7]. Following the treatment of Refs. [8–10], but replacing Laplace transforms by lattice generating functions, we introduce

$$\Psi(x, z) = \sum_{L=0}^{\infty} x^L \Xi_L(z), \tag{3.6}$$

which, by the bound (3.4) is analytic for $x < \frac{1}{2}\exp(-\beta\|\Phi\|)$. Then, if $x_0(z)$ is the radius of convergence of the series defining $\Psi(x)$ (which, of necessity, is determined by a singularity of $\Psi(x)$ on the real positive axis), we have

$$\beta p(z) a = -\ln x_0(z). \tag{3.7}$$

To construct the generating function $\Psi(x, z)$ we introduce, following Refs [8] and [9], the inter-cluster generating function

$$K(x) = \sum_{n=1}^{\infty}{}' x^n \exp[-\beta\varphi_2(na)], \tag{3.8}$$

where the prime denotes omission of distances, $r = na$, satisfying the cluster conditions. For the present model we thus have

$$K(x) = wx + x^3/(1-x) = x[w(1-x) + x^2](1-x)^{-1} \tag{3.9}$$

where

$$w = \exp[-\beta\varphi_2(a)] = e^{\beta v}. \tag{3.10}$$

From (2.8) we see, similarly, that the generating function for a single cluster is

$$H(x, z) = \sum_{l=1}^{\infty} z^l (x^2 y)^{l-1} e^{-\beta W(l)}, \tag{3.11}$$

where, by (2.9),

$$y = e^{-\beta\varphi_\infty} = e^{\beta W(2)}. \tag{3.12}$$

On summing over all possible clusters we find

$$\Psi(x, z) = (1-x)^{-1} + (1-x)^{-2} \sum_{m=1}^{\infty} [H(x, z)]^m [K(x)]^{m-1}. \tag{3.13}$$

The radius of convergence $x_0(z)$, is now determined either by the

Exterior Condition $\qquad H(x_0, z)\, K(x_0) = 1$ (3.14)

or, from (3.11) using (2.13), by the

Interior Condition $\qquad u = z x^2 y = 1.$ (3.15)

As in Ref. [8] it is convenient at this point to reexpress these formulae for the thermodynamics by setting

$$x = e^{-\beta p a}, \tag{3.16}$$

and defining a real function $u(x) \leqq 1$, through the implicit equation

$$\Upsilon[u(x)] = Q(x), \tag{3.17}$$

where

$$\Upsilon(u) = \sum_{l=1}^{\infty} u^l e^{-\beta W(l)} \quad \textit{and} \quad Q(x) = x^2 y / K(x). \tag{3.18}$$

The thermodynamics then follow from

$$\begin{aligned} \beta\mu(p) &= \ln z = \ln u(z) - 2\ln x - \ln y, \\ &= \ln u(x) + 2\beta p a + \beta v. \end{aligned} \tag{3.19}$$

Now $\Upsilon(u)$ is clearly a monotonic increasing functions of u which, as $u \to 1-$, approaches the value

$$\Upsilon(1) = \sum_{l=1}^{\infty} e^{-\beta W(l)} \leqq +\infty. \tag{3.20}$$

If $\Upsilon(1) < \infty$, and if

$$\begin{aligned} Q(x) &= y x (1-x)/[w(1-x) + x^2], \\ &> \Upsilon(1) \quad \text{for} \quad x_1 < x < x_2, \end{aligned} \tag{3.21}$$

then the root $u(x)$ "sticks" at the value 1 in the stated x-interval. In that case the density must remain constant at

$$\varrho_0 = \left(\frac{\partial p}{\partial \mu}\right)_\beta = \frac{1}{2a}, \quad \text{for} \quad x_1 \leqq x \leqq x_2. \tag{3.22}$$

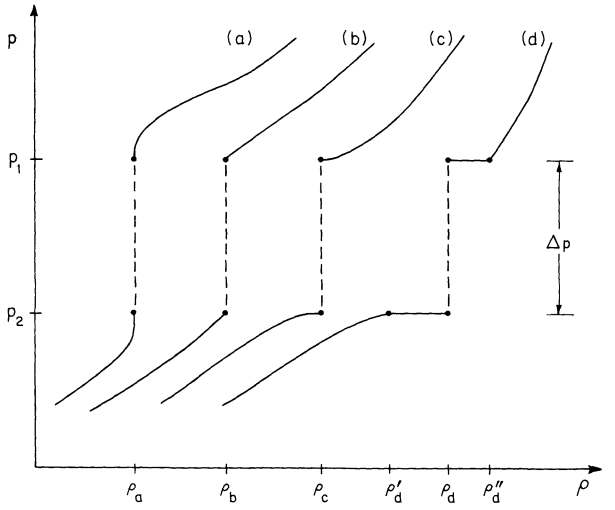

Fig. 1. Schematic discontinuous pressure-density isotherms. For the logarithmic model [defined by (3.26)] the various cases arise from (a) $1<\beta\varepsilon<1\frac{1}{2}$, (b) $\beta\varepsilon=1\frac{1}{2}$, (c) $1\frac{1}{2}<\beta\varepsilon<2$, and (d) $\beta\varepsilon>2$. Note the horizontal "two phase" regions in case (d)

Evidently, the pressure $p(\varrho)$ then exhibits a *discontinuity* at $\varrho=\varrho_0$ of magnitude

$$\Delta p = p_1 - p_2 = (\beta a)^{-1} \ln(x_2/x_1) > 0 . \tag{3.23}$$

(see Fig. 1).

Provided $w \neq 0$, which is ensured if v is finite, we see from the explicit expression in (3.21) that

$$\begin{aligned} Q(x) &\to 0 \quad as \quad x \to 0 \ (or\ p \to \infty), \\ &\quad and\ as \quad x \to 1 \ (or\ p \to 0). \end{aligned} \tag{3.24}$$

By continuity $Q(x)$ exhibits a maximum satisfying

$$Q_{\max} \geqq Q(\tfrac{1}{2}) = y/(1+2w) . \tag{3.25}$$

To demonstrate the existence of a pressure discontinuity it hence suffices to show that $W(l)$ can be chosen to satisfy:

X Discontinuity Condition

$$\Upsilon(1) = 1 + \sum_{l=2}^{\infty} e^{-\beta W(2)} < e^{\beta W(2)}/(1+2w) , \tag{3.26}$$

where we have used (3.12). For simplicity, we choose

Logarithmic Model

$$W(l) = \omega + \varepsilon \ln l \quad for \quad l \geqq 2, \quad with \quad \omega, \varepsilon > 0 , \tag{3.27}$$

so that

$$v_3 = \omega + \varepsilon \ln(4/3), \qquad v_l = \varepsilon \ln\{1 + [l(l-2)]^{-1}\}, \qquad (l > 3), \tag{3.28}$$

although many other choices are possible. If, in addition, we have

$$\beta\varepsilon - 1 > e^{-\beta\omega} > 0, \tag{3.29}$$

and

$$e^{\beta\omega} > 1 + 2w = 1 + 2e^{\beta v}, \tag{3.30}$$

we can construct the chain of inequalities

$$\begin{aligned} \Upsilon(1) &= 1 + e^{-\beta\omega} \sum_{l=2}^{\infty} l^{-\beta\varepsilon}, \\ &< 1 + e^{-\beta\omega} \int_1^{\infty} dl/l^{\beta\varepsilon} = 1 + e^{-\beta\omega}/(\beta\varepsilon - 1), \\ &< 2 < 2^{\beta\varepsilon} e^{\beta\omega}/(1 + 2w) = e^{\beta W(2)}/(1 + 2w). \end{aligned} \tag{3.31}$$

Finally then, we conclude that by choosing ω large enough, one can satisfy the discontinuity condition with the logarithmic model for any $\beta\varepsilon > 1$.

IV. Concluding Remarks

The above argument completes the proof of the existence of a pressure discontinuity in a class of lattice gases which satisfy the general conditions $\boldsymbol{T}$, $\boldsymbol{A}_0$, and $\boldsymbol{B}^*$. Conversely, since $W(l) \to \infty$ as $l \to \infty$, the supersummability condition $\boldsymbol{A}_0^+$ is necessarily violated. In the logarithmic model (3.27), however, it follows from (2.15) and (2.6) that the sum defining the norm $\|\Phi\|^+$ diverges only logarithmically fast. It is also interesting to enquire more closely into the possible shapes of the isotherm in the vicinity of the points of discontinuity. These may be found by noting that for the logarithmic models with $\beta\varepsilon > 1$ the expression (3.17) yields,

$$\Upsilon(u) \approx \Upsilon(1) - g(1-u)^{\sigma} \quad \text{as} \quad u \to 1-, \tag{4.1}$$

where $g(>0)$ depends only on $\beta\omega$ and $\beta\varepsilon$, and

$$\begin{aligned} \sigma &= \beta\varepsilon - 1, \quad \textit{for} \quad 1 < \beta\varepsilon < 2, \\ &= 1, \qquad \textit{for} \quad \beta\varepsilon > 2. \end{aligned} \tag{4.2}$$

On using this in (3.16) to solve for $u(x)$ with small $\Delta x = |x - x_j|$ $(j = 1 \text{ or } 2)$, we find

$$\ln u(x) \approx -h_j \Delta x^{1/\sigma}, \quad \text{as} \quad \Delta x \to 0, \tag{4.3}$$

where h_j is a constant. Substituting in (3.17) and differentiating to calculate $\varrho(p)$ finally yields, for $p > p_1$ or $p < p_2$,

$$\varrho(p) \approx \varrho_0 + f_j \Delta p^{\tau}, \quad \textit{as} \quad \Delta p = |p - p_j| \to 0, \quad (j = 1 \textit{ or } 2), \tag{4.4}$$

where f_j depends on $\beta\omega$ and $\beta\varepsilon$, while the exponent is given by

$$\begin{aligned} \tau &= (2-\beta\varepsilon)/(\beta\varepsilon-1), \quad \textit{for} \quad 1<\beta\varepsilon<2\,, \\ &= 0, \qquad\qquad\qquad \textit{for} \quad \beta\varepsilon>2\,. \end{aligned} \tag{4.5}$$

This result shows that the $\varrho(p)$ isotherm is continuous through the $p(\varrho)$ discontinuity for $\beta\varepsilon<2$, as indicated schematically for various cases in Fig. 1. On the other hand, when $\beta\varepsilon>2$ both $\varrho(p)$ *and* $p(\varrho)$ are discontinuous functions (see Fig. 1 d).

The physical mechanism of the pressure discontinuity in the models discussed is evidently the "condensation" of the gas into a "rigid" crystal of fixed density. Only when the pressure is increased sufficiently to "crush" the crystal does the isotherm resume its continuous variation. In the present, simple models the crystal is essentially completely rigid and has no internal degrees of freedom. However, at the cost of somewhat more elaborate cluster interaction forces one could produce a pressure discontinuity associated with a crystal of constant *limiting* density but which, more realistically, allowed local internal density fluctuations. Along the same lines it seems likely that one could produce analogous, one-dimensional *continuum* models with a pressure discontinuity.

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