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A Mechanical Definition of the Thermodynamic Pressure

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A dynamical definition of pressure for grand-canonical Gibbs measures in bounded regions Λ is rigorously discussed: It measures the momentum transferred to the walls of the container by the elastically colliding particles. The local pressure $P(r, \partial\Lambda)$ so obtained is proportional to the temperature and the local density at the boundaries of Λ. This allows us to obtain a rigorous proof of the virial theorem of Clausius. In this picture the thermodynamic pressure $P^d(\Lambda)$ is obtained as the average of $P(r, \partial\Lambda)$ on $\partial\Lambda$. Its relationship with the usual equilibrium pressure $P^{eq}(\Lambda) = (\beta|\Lambda|)^{-1} \ln Z_\Lambda$ (Z_Λ is the grand-canonical partition function) is then discussed. In the particular case in which the regions Λ are spheres, it is shown that $P^d(\Lambda)$ converges in average so that, if the limit of $P^d(\Lambda)$ exists, it equals P^{eq}, the thermodynamic limit of the equilibrium pressure $P^{eq}(\Lambda)$. Finally, convergence of $P^d(\Lambda)$ is proven to hold in the particular case of one-dimensional hard cores in the absence of phase transitions.

KEY WORDS: Rigorous statistical mechanics; Gibbs states; pressure; virial theorem of Clausius; finite-volume dynamics; special flows under a function.

1. INTRODUCTION AND MAIN RESULTS

In this paper we discuss a definition of the thermodynamic pressure which involves purely mechanical considerations.

We study classical continuous systems in bounded regions Λ and we

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assume that their equilibrium states are described by grand-canonical Gibbs measures. The usual assumption in statistical mechanics[1] for the pressure P_Λ^{eq} is

$$P_\Lambda^{eq} = (|\Lambda|\beta)^{-1} \ln Z_\Lambda \tag{1}$$

where $\beta^{-1} = kT$ and Z_Λ is the grand-canonical partition function. [Actually, Eq. (1) can be derived from thermodynamic and information theory considerations.[1]]

On the other hand, the pressure is physically defined as the external action necessary to constrain the system in a bounded region. It is a standard procedure[2] in the kinetic theory of gases to identify it as the momentum transferred from the colliding particles to the walls in the limit in which these are assumed to be perfectly elastic. This opens the way to many classical theorems which relate the pressure to other thermodynamic observables, as in the virial theorem of Clausius.[2,3]

It is the purpose of this paper to examine this procedure in the framework of rigorous statistical mechanics and to discuss the relationship between the so-defined dynamical pressure P^d and the usual equilibrium pressure P^{eq}, Eq. (1).

The first problem one is confronted with is the definition of dynamics for particles moving in nonsmooth fields. More precisely, we have the following.

Definition 1.1. We study a system of point particles with mass m in $\mathbb{R}^\nu$ pairwise-interacting via a stable, tempered[1] C^2 potential $\varphi(r)$. The corresponding (grand-canonical) Gibbs state for the bounded (Lebesgue-measurable) region Λ is the probability measure μ_Λ on the phase space X_Λ (see Definition 2.1).

The formal differential equations of motion are

$$m \frac{d^2}{dt^2} q_i(t) = -\sum_{j \neq i} \frac{\partial}{\partial q_i} \varphi(|q_i - q_j|) + \text{elastic collisions on } \partial\Lambda \tag{2}$$

$$q_i(0) = q_i, \qquad \dot{q}_i(0) = p_i/m \qquad (q_i \cdots q_n)(p_i \cdots p_n) \in X_\Lambda \tag{3}$$

Problems arise from the impulsive forces due to collisions against the elastic walls. They are studied in Ref. 4, where the following theorem is proved (an outline of the proof is given in the appendix).

Theorem 1.1. Let the region Λ be regular (see Definition 2.1). Then there exists a set of initial configurations with full μ_Λ measure for which a time evolution $S(t)$ is defined for $t \in \mathbb{R}$. $S(t)$ satisfies the following properties:

(i) No particle ever hits $\partial\Lambda$ in its singular region. For any finite time interval a bounded number of collisions occurs. Between collisions the evolution satisfies the differential equations of motion and during collisions the particles are elastically reflected, Eqs. (2) and (3).

(ii) μ_Λ is S-invariant.

By use of Theorem 1.1 we can define the following function:

$$\pi_\Omega(t, x) = \sum_{0 \leqslant t' \leqslant t} \sum_{i \in \mathscr{G}_\Omega^{(t')}} 2[S(t')p_i] n_\Lambda [S(t')q_i]$$

where

$$\Omega \subseteq \partial\Lambda, \qquad \mathscr{G}_\Omega(t) = \{i \mid S(t)q_i \in \Omega, q_i \in \Lambda\} \tag{4}$$

and $n_\Lambda(q)$ is the unit inward vector orthogonal to $\partial\Lambda$ in $q \in \partial\Lambda$. Therefore $\pi_\Omega(t, x)$ gives the total momentum transferred to the subregion Ω of $\partial\Lambda$ by the particles of x due to collisions in the time interval $(0, t)$.

Theorem 1.2. For every $t \geqslant 0$ and every regular $\Omega \subseteq \partial\Lambda$ the function $\pi_\Omega(t, x)$ is μ_Λ-integrable and there exists in $\partial\Lambda$ a function $P(r, \partial\Lambda)$ not depending on Ω such that

$$t^{-1} \int_{X_\Lambda} d\mu_\Lambda(x) \pi_\Omega(t, x) = \int_\Omega (dr)^\perp P(r, \partial\Lambda) \tag{5}$$

where $(dr)^\perp$ is the orthogonal projection of dr on $\partial\Lambda$. Therefore $P(r, \partial\Lambda)$ is the dynamical local pressure in $r \in \partial\Lambda$. Further if $\rho(r, \Lambda)$ represents the local density, then

$$P(r, \partial\Lambda) = \rho(r, \Lambda) \tag{6}$$

By Theorem 1.2 we obtain for the dynamical pressure on $\partial\Lambda$

$$P^d = (|\partial\Lambda|)^{-1} \int_{\partial\Lambda} (dr)^\perp P(r, \partial\Lambda) \tag{7}$$

The same procedure we used to "measure" the dynamical pressure can be applied also in the interior of the system. The idea is to insert as a measuring apparatus a potential field which separates the particles inside some subregion Λ' of Λ from those outside. We theoretically perform the limit in which the size of the inserted walls becomes negligibly small. The momentum transferred from the particles inside Λ' to the walls $\partial\Lambda'$ is usually called the kinetic part of the pressure inside the system. It is in fact generally different from the actual pressure P^d. The difference measures the force exerted by the particles outside Λ' on Λ' and it is usually related to the stress tensor of the system.[2] We remark that the above well-known procedure has a geometrical more than a physical meaning because it amounts to considering the size of the elastic macroscopic walls $\partial\Lambda'$ much smaller than the range of the microscopic forces between particles.

From a mathematical point of view, however, the above limit is perfectly defined. We introduce equations of motion as in Eq. (2) where we consider also elastic collisions on $\partial\Lambda'$. The complete analog of Theorem 1.1 is obtained in the assumption of regularity for Λ'; a proof is given in Section 2. The momentum transferred to Ω is measured by the function $\tilde{\pi}_\Omega(t, x)$ defined as in Eq. (4), reading Ω as a subregion of $\partial\Lambda'$. We then have the following result.

Theorem 1.3. For every $t \geqslant 0$ and every regular $\Omega \subseteq \partial\Lambda'$ the function $\tilde{\pi}_\Omega(t, x)$ is μ_Λ-integrable and there exists a function on Λ, $P(r, \Lambda)$ not depending on Λ', such that

$$t^{-1} \int_{X_\Lambda} d\mu_\Lambda(x)\tilde{\pi}_\Omega(t, x) = \int_\Omega (dr)^\perp P(r, \Lambda) \tag{8}$$

and

$$\beta^{-1}P(r, \Lambda) = \rho(r, \Lambda) \tag{9}$$

Theorem 1.3 somehow extends the results of Theorem 1.2 by proving that proportionality between local density, temperature, and pressure holds in the whole system as far as the kinetic pressure is considered.

As a consequence of the definition of the pressure P^d we gave via Theorem 1.2 (which directly related the thermodynamic pressure to the real external force acting on the system), we are able to derive a rigorous proof of the virial theorem of Clausius in its original [Eq. (10)] and in its modified [Eq. (11)] form.

Theorem 1.4. Let Λ be regular, let $\rho(r_1, r_2)$ be the two-particle correlation function; then

$$\int_{\partial\Lambda} (dq)^\perp qn(q)P(q, \partial\Lambda) + \tfrac{1}{2} \int_{\Lambda^2} dq_1 dq_2\, \rho(q_1, q_2)(q_2 - q_1)(\partial/\partial q_1)\varphi(|q_1 - q_2|) = -2\langle T\rangle \tag{10}$$

$$\int_{\partial\Lambda} (dq)^\perp qn(q)P(q, \partial\Lambda) + \tfrac{1}{2} \int_{\partial\Lambda} (dq_1) \int_\Lambda dq_2 \rho(q_1, q_2)(q_2 - q_1)(\partial/\partial q_1)\varphi(|q_1 - q_2|) = -2\langle T\rangle \tag{11}$$

$\langle T\rangle$ is the mean kinetic energy. In the case the region Λ is a sphere $P(r, \partial\Lambda) = P^d$, by symmetry, so that, if ν is the dimension of the space,

$$\int_{\partial\Lambda} (dq)^\perp qn(q)P(q, \partial\Lambda) = P^d \nu$$

which inserted into Eqs. (10) and (11) gives them their more usual form.

An important well-known consequence of the previous definition of pressure as P^d (other than the above derivation of the virial theorem) is the quite simple interpretation of the equation of state for the system, as it relates surface to volume effects. In fact, since P^d is determined by the density near the surface, an increase in the mean density at constant temperature is reflected in a variation of the pressure according to the way the local densities change: The regions of high compressibility are determined by situations in which the increase is realized largely in the neighborhood of the boundaries, while independence is apparent whenever the increase in density is localized far from the surface $\partial\Lambda$.

In order to give full meaning both to the definition of pressure P^d and to its consequences we have seen so far, we need to discuss its relationship with the equilibrium pressure P^{eq} defined in Eq. (1). We would expect them to be equal, at least in the thermodynamic limit, and this will be the argument of the remaining part of this section.

In order to study the thermodynamic limit for $P^d(\Lambda)$, we avoid all the complications connected with the possible changes in shape of $\partial\Lambda$ by considering the regions Λ to be spheres centered in the origin of $\mathbb{R}^\nu$ and invading the whole space. In this framework we obtained the following partial answer to the above problem.

Theorem 1.5. Let v be the volume of the sphere Λ_v; then:

(i) Let $P^{eq} = \lim_{v\to\infty} P^{eq}(\Lambda_v)$,

$$P^{eq} = \lim_{v\to\infty} v^{-1} \int_0^v dv'\, P^d(\Lambda_{v'}) \tag{12}$$

As a consequence, whenever the thermodynamic limit exists for $P^d(\Lambda_v)$, it equals P^{eq}. Further, there always exist opportune sequences of spheres Λ_n invading $\mathbb{R}^\nu$ such that $\lim P^d(\Lambda_n) = P^{eq}$.

(ii) In the case our system is a gas of one-dimensional hard rods in $\mathbb{R}$ of length a with pair potential $\varphi(r)$ given by

$$\varphi(r) = \begin{cases} \infty & \text{for } 0 \leqslant r \leqslant a \\ C^2 & \text{for } r \geqslant a \\ \text{there exist } D \text{ and } R_0 \text{ such that } |\varphi(r)| \leqslant Dr^{-2+\epsilon},\ r \geqslant R_0,\ \epsilon > 0 \end{cases} \tag{13}$$

let $\Lambda_l = [0, l]$; then

$$\lim_{l\to\infty} P^d[(0, l)] = P^{eq}$$

From Theorem 1.4 it appears that the real problem is to show the existence of the thermodynamic limit for $P^d(\Lambda)$ and this, by Theorem 1.2, corresponds to the study of the one-particle correlation function near the boundaries in the thermodynamic limit. In the case treated in Theorem 1.5(ii) the surface effects are fully described by a semiinfinite equilibrium measure as introduced and studied in Ref. 5. It would be interesting also in this respect, therefore, to carry out analogous studies for very long-range forces. In this case a phase transition can be present and different equilibrium measures can exist at the same temperature and chemical potential.

In Section 2 we give the proofs of the theorems presented in this section, and in the appendix we sketch the lines of the proof of Theorem 1.1.

2. PROOFS

In Definitions 2.1–2.3 below we recall some well-known definitions and we establish notations needed in the sequel.

Definition 2.1. Let Λ be a bounded Lebesgue-measurable set in $\mathbb{R}^\nu$; then the phase space X_Λ and the grand-canonical Gibbs measure are defined as

$$X_\Lambda = \bigcap_{0}^{\infty}{}_n (\Lambda \times \mathbb{R}^\nu)^n \qquad \left(\bigcap \text{ denotes disjoint union}\right) \tag{14}$$

$$\mu_\Lambda(dx) = \sum_{0}^{\infty}{}_n (n!)^{-1}\, d(q)_n{}^\Lambda \cdot d(p)_n \exp\{\beta[\mu n - H((q)_n(p)_n)]\} Z_\Lambda^{-1} \tag{15}$$

$$(q)_n = q_1 \cdots q_n, \qquad (p)_n = p_1 \cdots p_n$$

$$d(q)_n{}^\Lambda = dq_1 \cdots dq_n\, \chi_\Lambda(q_1) \cdots \chi_\Lambda(q_n)$$

$$(\chi_\Lambda \text{ is the characteristic function of } \Lambda)$$

$$d(p)_n = dp_1 \cdots dp_n$$

$$H((q)_n(p)_n) = (2m)^{-1} \sum_{1}^{n}{}_i p_i{}^2 + \tfrac{1}{2} \sum_{i \neq j} \varphi(|q_i - q_j|) = T[(p)_n] + U[(q)_n]$$

$$Z_\Lambda = \sum_{0}^{\infty}{}_n z^n \int_{\Lambda^n} d(q)_n{}^\Lambda (n!)^{-1} \exp[-\beta U((q)_n)]$$

$$\dot{z} = (2\pi m \beta^{-1})^{\nu/2} e^{\beta\mu}$$

We will always consider regions Λ such that the boundaries are closures of a disjoint union of a finite number of open, regular (with continuous normal derivative) subregions. We require that the normal derivative never has discontinuities larger than $\pi/2$. By Λ' it will be denoted a region strictly contained in Λ and at finite distance from $\partial\Lambda$.

Definition 2.2. Let $X_\Lambda^{(1)}$ be the one-particle phase space:

$$X_\Lambda^{(1)} = \{\eta | \eta = (q, p), q \in \Lambda, p \in \mathbb{R}^\nu\} \tag{16}$$

In $X_\Lambda^{(1)}$ the following surfaces will be considered:

$$\Sigma = \Sigma^{\text{ext}} \cup \Sigma' \tag{17}$$

where

$$\Sigma^{\text{ext}} = \{\xi \in X_\Lambda^{(1)} | \xi = (q,p), \quad q \in \partial(\Lambda - \Lambda')p_{\Lambda-\Lambda'}(\xi) > 0\}$$

$$\Sigma' = \{\xi \in X_\Lambda^{(1)} | \xi = (q,p), \quad q \in \partial\Lambda', p_{\Lambda'}(\xi) > 0\}$$

$$p_\Delta(\xi) = p \cdot n_\Delta(\xi), \qquad \xi = (q,p) \tag{18}$$

$$n_\Delta(\xi) = \text{inward unit vector orthogonal to } \partial\Delta \text{ in } q \in \partial\Delta \tag{19}$$

On Σ we consider the measure σ as

$$\sigma(d\xi) = (dq\, dp)^\perp m^{-1} p(\xi) \tag{20}$$

where $(dq\, dp)^\perp$ is the orthogonal projection of $(dq\, dp)$ on Σ.

By Ω we denote an open, continuous surface contained in $\partial\Lambda'$ or $\partial(\Lambda - \Lambda')$.

Definition 2.3. Let $\mathscr{T}(X_\Lambda)$ be the set of configurations for which no particle is in $\partial\Lambda$ and $\partial(\Lambda - \Lambda')$.

We assume Theorem 1.1 already proven. We refer to Ref. 4 for a detailed demonstration: In the appendix, we give the main ideas by actually proving the stronger statement Theorem A.1.

It is convenient to introduce special notations for the sets of configurations of interest in Theorems 1.2 and 1.3. This is done in the following definition.

Definition 2.4. Let Ω be as in Definition 2.2; then

$$X^\Omega = \{x = (q)_n(p)_n \in X_\Lambda | \text{ (i) } \forall t \in \mathbb{R} \text{ no more than one particle of } S(t)x \text{ is in } \Omega, \text{ (ii) } \exists t_0 \geqslant 0, x_0 = (u, \xi) = (q^0)_n(p^0)_n \text{ such that } S(t_0)x_0 = x \text{ with } u \in \mathscr{T}(X_\Lambda), \xi \in \Omega\} \tag{21}$$

For $x \in X^\Omega$ we pose

$$x = (x_0, t) = (u, \xi, t) \tag{22}$$

where t is the minimum time for which the representation (22) holds. We pose

$$\mathscr{B}^\Omega = \{x \in X^\Omega | x = (u, \xi, 0)\colon \xi \in \Omega, u \in \mathscr{T}(X)_\Lambda\} \tag{23}$$

and we call it the Ω-base of the flow $S(t)$. The following function is defined on $\mathscr{B}^\Omega$:

$$\tau^\Omega(x) = \min\{t | S(t)x \in \mathscr{B}^\Omega, x \in \mathscr{B}^\Omega, t > 0\} \tag{24}$$

Theorems 1.2 and 1.3 will be straightforward consequences of the representation of the flow $S(t)$ given in the following theorem, which, in turn, is a corollary of Theorem A.1.

Theorem 2.1. We assume the pair potential φ as in Definition 1.1 and the regions Λ and Λ' regular in the sense specified in Definition 2.1. Then the following hold:

(i) The set X^{Ω} is μ_Λ-measurable and it has the same measure as the set X^{coll}, i.e., the configurations for which at some time a particle hits the surface of Ω.

(ii) the measure μ_Λ restricted to X^{Ω} has the expression

$$\mu_\Lambda(dx) = \nu^{\Omega}(dy)\cdot dt \equiv \mu_\Lambda(du)\cdot\sigma(d\xi)\cdot dt\cdot W(y,\xi)\theta[\tau^{\Omega}(y) - t] \tag{25}$$

where $x = (u, \xi, t)$ was defined in Eq. (22); $y = (u, \xi) \in \mathscr{B}^{\Omega}$ in Eq. (23); τ^{Ω} in Eq. (24); and

$$W(y,\xi) = \exp\{-\beta I(\xi, u) - \beta T(\xi) + \beta\mu\}$$

$$I(\xi, u) = \sum_{\substack{i \\ q_i\in u}} \varphi(|q_i - q|); \qquad \xi = (q, p) \tag{26}$$

and $\theta(s) = 0$ if $s < 0$ and $\theta(s) = 1$ if $s \geqslant 0$. The function τ^{Ω} is ν^{Ω}-measurable.

(iii) The transformation $S(t)$ determines ν^{Ω}-modulo zero a transformation T^{Ω} on $\mathscr{B}^{\Omega}$,

$$T^{\Omega}y = S[\tau^{\Omega}(y)]y \tag{27}$$

which preserves ν^{Ω}.

(iv) As a consequence of the above, the dynamical system $(X^{\Omega}, \mu_\Lambda, S(t))$ is represented as a flow under the function τ^{Ω} on the base $\mathscr{B}^{\Omega}$ with transformation T^{Ω}.

Theorem 2.1 suggests that we study the function $\pi(t, x)$ as a function of x for every fixed t. Then the special form of μ_Λ given in Eq. (25) will imply the desired linearity in t of $\int \mu_\Lambda(dx)\cdot\pi(x, t)$. In order to carry out this program, it is convenient to represent the flow $S(t)$ on X^{Ω} as a translation upward on $\mathscr{B}^{\Omega} \times \mathbb{R}^+$, by identifying points of the latter space as follows.

Definition 2.5. We pose

$$\tau_0(y) = 0, \qquad \tau_n(y) = \tau^{\Omega}(T^{n-1}y) + \tau_{n-1}(y), \qquad n \geqslant 1, \qquad T^{\Omega} = T \tag{28}$$

$$\mathscr{M}_n = \{(y, t) \in \mathscr{B}^{\Omega} \times \mathbb{R}^+ | \tau_{n-1}(y) \leqslant t < \tau_n(y)\} \tag{29}$$

$$\psi_n\colon\ X^{\Omega} \to \mathscr{M}_n, \qquad \psi_n[(y, t)] = (y^n, t^n) \tag{30a}$$

$$T^{n-1}y^n = y, \qquad t^n - \tau_{n-1}(y^n) = t \tag{30b}$$

ψ_n carries the measure μ_Λ on X^{Ω} into the measure $\hat\mu_n$ on $\mathscr{M}_n$ via

$$\int_{X^{\Omega}} \mu_\Lambda(dx) f(x) = \int_{\mathscr{M}_n} \hat\mu_n[d(\psi_n x)] f_n[\psi_n x], \qquad f_n[\psi_n x] = f(x) \tag{31}$$

We explicate Eq. (31), and use Eq. (25) and the invariance of ν^{Ω} under T^{Ω} so that by applying the Fubini theorem we have

$$\hat\mu_n[d(y, t)] = \nu^{\Omega}(dy)\cdot dt\cdot\chi[\tau_{n-1}(y), \tau_n(y)](t) \tag{32}$$

χ_I is the characteristic function of the interval I.

By Theorem 1.1(i), $\bigcup_1^\infty \mathscr{M}_n = \mathscr{B}^\Omega \times \mathbb{R}^+$ μ_Λ modulo zero, so that the above defines a measure $\hat{\mu}$ on $\mathscr{B} \times R^+$ s.t. $\hat{\mu}|_{\mathscr{M}_n} = \hat{\mu}_n|\mathscr{M}_n$ and $d\hat{\mu} = d\nu^\Omega \cdot dt$.

In the next lemma we represent the function $\pi(t, x)$ in $\{\mathscr{B}^\Omega \times \mathbb{R}^+, \hat{\mu}\}$ and obtain an explicit expression for its integral.

Lemma 2.1. To every positive measurable (possibly infinite) function f on $\mathscr{B}^\Omega \times \mathbb{R}^+$ there corresponds a positive function h_f on X^Ω defined by

$$h_f(x) = \sum_1^\infty f[\psi_n x] \tag{33}$$

such that

$$\int_{\mathscr{B}^\Omega \times \mathbb{R}^+} \hat{\mu}(dx) f(x) = \int_{X^\Omega} \mu_\Lambda(dx) h_f(x) \tag{34}$$

In particular, $\pi(\bar{t}, x)$ is obtained as in Eq. (33) from the function

$$f[(y, t)] = f[((u, \xi), t)] = 2p_\Omega(\xi)\theta(t - \bar{t}) \tag{35}$$

where $p_\Omega(\xi)$ is defined in Eq. (18). Therefore $\pi(t, x)$ is measurable and by Eq. (34) we have

$$\int_{X^\Omega} d\mu_\Lambda(x)\pi(\bar{t}, x) = \bar{t} \int_{\mathscr{B}^\Omega} \nu^\Omega(dy)\, 2p_\Omega(\xi), \qquad y = (u, \xi) \tag{36}$$

Proof. Measurability of h_f and Eq. (34) are consequence of Fatou's lemma (see, for instance, Ref. 6, III.6.17). Measurability of f in Eq. (35) is derived by Fubini's theorem and measurability of $p_\Omega(\xi)$ in ν^Ω and $\theta(t - \bar{t})$ in dt.

Proof of Theorems 1.2 and 1.3. Both theorems are now a direct consequence of Eq. (36). We write out explicitly ν^Ω as in Eqs. (25) and (26) so that we have from Eq. (36)

$$\begin{aligned}
t^{-1} &\int \mu_\Lambda(dx)\, \pi_\Omega(t, x) \\
&= \int \mu_\Lambda(du) \int \sigma(d\xi)\, 2p(\xi) \exp\{-\beta[T(\xi) - \mu + I(\xi, u)]\} \\
&= \int \mu_\Lambda(du) \int_\Omega (dq)^\perp \Big\{ \int_0^\infty dp \exp[-\beta(2m)^{-1}p^2]\, 2p^2(m)^{-1} \\
&\qquad \times (\exp \beta\mu)(2\pi m\beta^{-1})^{\nu - 1/2} \Big\} \exp - \beta I(q, u) \\
&= z(\beta)^{-1} \int_\Omega (dr)^\perp \int \mu_\Lambda(du) \exp[-\beta I(\xi, u)]
\end{aligned}$$

so that the theorems are proved with

$$P(r, \Lambda) = z(\beta)^{-1} \int \mu_\Lambda(dx) \exp[-\beta I(r, x)] \equiv (\beta)^{-1} \rho(r, \Lambda) \tag{37}$$

Proof of Theorem 1.4. Theorem 1.4 is derived by use of Lemma 2.1 in the classical proof of the virial theorem of Clausius as given by Milne[7]. Let x be a configuration for which dynamics is defined as in Theorem 1.1. We then write Eq. (1) for the particle $q_i \in x$ at a time in which no particle is colliding on $\partial\Lambda$. We multiply by q_i, sum over all the particles, integrate in time, for the time interval $(0, t)$, assuming that at both times 0 and t no particle is hitting $\partial\Lambda$, and obtain

$$\begin{aligned} -m \sum_{0 \leqslant t' \leqslant t} \sum_{i \in \mathscr{G}_{\partial\Lambda}(t')} q_i(t')\, \Delta\dot{q}_i(t') + \tfrac{1}{2}m \sum_{i=1}^{n} (d/dt)(q_i^2) \\ -2 \int_0^t dt' \sum_{i=1}^{n} \tfrac{1}{2} m\dot{q}_i^2(t') = \int_0^t dt' \sum_{i=1}^{n} F_i(t') q_i(t') \end{aligned} \tag{38}$$

where $\mathscr{G}_{\partial\Lambda}(t')$ is defined below Eq. (4) and

$$F_i(t') = \sum_{j \neq i} (\partial/\partial q_i)\varphi[|q_i(t') - q_j(t')|]$$

The function $\phi(x, t)$,

$$\phi(x, t) = \sum_{0 \leqslant t' \leqslant t} \sum_{i \in \mathscr{G}_{\partial\Lambda}(t')} q_i(t') \Delta\dot{q}_i(t')$$

is the analog of $\pi(x, t)$, so that we can again apply Lemma 2.1, and the function corresponding to $\phi(x, t)$, as in Eq. (35), is

$$g[(y, t)] = g[(u, \xi), t] = 2p_{\partial\Lambda}(\xi) q_{\partial\Lambda}(\xi) \theta(t' - t) \tag{39}$$

We can therefore average Eq. (38) with respect to μ_Λ. Using the invariance of μ_Λ, we finally obtain Eq. (10) with

$$\rho(q_1, q_2) = Z^{-1} \sum_{n=2}^{\infty} z^n[(n-2)!]^{-1} \int_{\Lambda^{n-2}} dq_3 \dots dq_n \, e^{-\beta U(q_1 \cdots q_n)}$$

Equation (11) is derived similarly. It is just sufficient first to sum all the equations of motion for the different particles, so that the interparticle forces disappear. We then multiply by the position of the center of mass, integrate over t, and average with respect to μ_Λ.

Proof of Theorem 1.5. (i) Let s be the radius of the sphere Λ_s centered at the origin of $\mathbb{R}^\nu$ and let v_s be its volume. Let $Z_s = Z(\Lambda_s)$; then

$$\frac{d}{ds}\ln Z_s = (|\partial\Lambda_s|)^{-1} Z_s^{-1}\frac{d}{ds}Z_s$$

$$= (|\partial\Lambda_s|)^{-1} Z_s^{-1}\sum_1^{\infty}{}_n (n!)^{-1} z^n n \int_{(\Lambda_s)^{n-1}} d(q)_{n-1}$$

$$\times \exp\{-\beta U[(q)_{n-1}]\}\int_{\partial\Lambda_s}(dr)^{\perp}\exp\{-\beta I(r,(q)_{n-1})\}$$

$$= (|\partial\Lambda_s|)^{-1} z\int_{\partial\Lambda_s}(dr)^{\perp}\sum_0^{\infty}{}_n z^n(n!)^{-1}$$

$$\times\int_{(\Lambda_s)^n} d(q)_n\exp\{-\beta U[(q)_n]-\beta I(r,(q)_n)\}Z_s^{-1}$$

$$= (|\partial\Lambda_s|)^{-1} z\int_{\partial\Lambda_s}(dr)^{\perp}\int_{X_{\Lambda_s}} d\mu_s(x)\exp[-\beta I(r,x)]$$

$$= (|\partial\Lambda_s|)^{-1}\int_{\partial\Lambda_s}(dr)^{\perp}\beta P(r,\Lambda_s) = \beta P^d(\Lambda_s) \tag{40}$$

To obtain Eq. (40), we used the stability of the interaction, Definition 1.1, to ensure uniform convergence of the series. From Eq. (40) we have

$$(v)^{-1}\int_0^v dv'\,P^d(\Lambda_{v'}) = (\beta v)^{-1}\ln Z_v \xrightarrow[v\to\infty]{} P^{\mathrm{eq}} \tag{41}$$

so that (i) is proved using the continuity of $P^d(\Lambda_v)$ on v.

(ii) The considerations leading to Theorem 1.2 can be rephrased with minor modifications in the case the particle are hard rods. The point is that the analog of Theorem A.1 can be similarly proved by constructing the base of the special flow as the surface of the phase space union of $\mathscr{B}^{\Sigma}$ and of that region in which more rods are contiguous. Therefore we assume without proof that the analog of Eq. (37) holds, so that with the notations $\Lambda_L = [0, L]$ and $\Lambda' = \Lambda_L$ we obtain for $P^d_{\Lambda_L}$

$$P^d_{\Lambda_L} = (\beta)^{-1} z\int_{X_{\Lambda_L}}\mu_{\Lambda_L}(dx)\exp[-\beta I(0,x)]$$

Lemma 9 of Ref. 5 allows us to perform the thermodynamic limit for $L\to\infty$ in Eq. (40) so that

$$\lim_{L\to\infty} P^d_{\Lambda_L} = P^d = \beta^{-1} z\int_{X(\mathbb{R}^+)}\nu(dx)\exp[-\beta I(0,x)] \tag{42}$$

where the measure ν is defined in Lemma 1 of Ref. 5 and represents the semi-infinite thermodynamic limit of Gibbs measures. The important point for our purposes is that the following property holds for ν (Lemma 9, Ref. 5):

$$\exp(\beta r P^{\text{eq}}) = \sum_{0}^{\infty}{}_n (n!)^{-1} z^n \int_{(-r,0)^n} d(q)_n \exp\{-\beta U[(q)_n]\} \times \int_{X(\mathbb{R}^+)} \nu(dx) \exp\{-\beta I[(q)_n, x]\} \tag{43}$$

Therefore by Eqs. (42) and (43)

$$\begin{aligned}\beta P^{\text{eq}} &= \lim_{r\to 0} r^{-1} \sum_{1}^{\infty}{}_n (n!)^{-1} \int_{(-r,0)^n} d(q)_n \exp\{-\beta U[(q)_n]\} \\ &\quad\times \int_{X(\mathbb{R}^+)} (dx) \exp\{-\beta I[(q)_n, x]\} \\ &= \lim_{r\to 0} r^{-1} z \int_{-r}^{0} dq \int_{X(\mathbb{R}^+)} \nu(dx) \exp\{-\beta I(q, x)\} \\ &= z \int_{X(\mathbb{R}^+)} \nu(dx) \exp[-\beta I(0, x)] \\ &= \beta P^d\end{aligned}$$

APPENDIX

Here we sketch the proof of Theorem 1.1. In the proof a special representation of the time evolution flow is introduced and as a corollary Theorem 2.1 is also obtained. A detailed analysis can be found in Ref. 4. We first introduce some notations and then we shall give the theorem.

Definition A.1. For any configuration in $\mathscr{T}(X_\Lambda)$ (Definition 2.3), there exists a time interval $(-t', t'')$, $t', t'' > 0$, such that a time evolution $S^0(t)$ is determined as a solution of Eqs. (1) and (2) with no particles colliding on $\partial\Lambda'$ and $\partial(\Lambda - \Lambda')$. This naturally splits X_Λ into three sets:

$$X^\Sigma = \{(q)_n(p)_n \in \mathscr{T}(X_\Lambda) | \exists t > 0, (q^0)_n(p^0)_n\text{: } S^0(t) \text{ is defined on } (q^0)_n(p^0)_n \quad\text{and}\quad S^0(t)[(q^0)_n(p^0)_n] = (q)_n(p)_n\} \tag{A.1}$$

$$(q^0)_n(p^0)_n = (u, \xi), \qquad u \in \mathscr{T}(X_\Lambda), \qquad \xi \in \Sigma$$

$$X^0 = \{(q)_n(p)_n | S^0(t) \text{ is defined on } (q)_n(p)_n \text{ for every } t \in \mathbb{R}\} \tag{A.2}$$

$$\bar{X} = \text{complement in } X_\Lambda \text{ of } X^\Sigma \cup X^0 \tag{A.3}$$

As in Eqs. (23) and (24), we describe X^Σ giving its base $\mathscr{B}^\Sigma$ and the function τ^Σ so that if $x \in X^\Sigma$, then

$$x = (y, t), \qquad t < \tau^\Sigma(y), \qquad S^0(t)y = x \tag{A.4a}$$

$$y = (u, \xi), \qquad u \in \mathscr{T}(X_\Lambda), \qquad \xi \in \Sigma \tag{A.4b}$$

Theorem A.1. Let the pair interaction be defined as in Definition 1.1, and the regions Λ and Λ' be regular in the sense of Definition 2.1; then

(i) The sets X^Σ, X^0, $\bar{X}$ are μ_Λ-measurable and $\mu_\Lambda(\bar{X}) = 0$.

(ii) The function τ^Σ is measurable with respect to the measure $\mu_\Lambda \times \sigma$ on $\mathscr{B}^\Sigma$ and if μ_Λ denotes the restriction of μ_Λ to X^Σ, we have

$$\mu_\Lambda(dx) = \nu^\Sigma\, dt \equiv \mu_\Lambda(du)\cdot\sigma(d\xi)\, dt\, W(y, \xi)\theta[\tau^\Sigma(y) - t] \tag{A.5}$$

where W, I, and θ are defined as in Eq. (25).

(iii) Let $S^0(\tau^\Sigma(y))y = T^\Sigma y$ be identified with the elastically reflected configuration. Then in the complement with respect to $\mathscr{B}_\Sigma$ of a set of null measure T^Σ and all its powers are ν^Σ measure-preserving transformations of $\mathscr{B}^\Sigma$ onto itself.

(iv) Let

$$\mathscr{N} = \{y \in \mathscr{B}^\Sigma | \sum_n^{\infty}{}_{1} \tau[(T^\Sigma)^{n-1}y] < +\infty\} \tag{A.6}$$

then $\nu^\Sigma(\mathscr{N}) = 0$, so that the transformation T^Σ determines a μ_Λ-preserving flow $S^\Sigma(t)$ of X^Σ onto itself represented as a transformation T^Σ on $\mathscr{B}^\Sigma$ under the function τ^Σ.

Proof. In Ref. 4 a connected surface is studied; however, in that proof such a hypothesis is actually never used, so that it applies directly to our case. Therefore here we only recall the main arguments.

Measurability of X^Σ follows from the topological properties of the flow $S^0(t)$ together with the regularity of Σ and of the measure μ_Λ in the topological space X_Λ. By the same arguments it is proven that τ^Σ is measurable. Equation (A.5) is then derived from the invariance of μ_Λ on $S^0(t)$, (4,8) and at the same time it is proven that $\mu_\Lambda(\bar{X}) = 0$.

At this point T^Σ can be defined and (iii) is proven as a consequence of the explicit construction of ν^Σ together with the fact that the transformation which identifies a configuration in $S^0[\tau^\Sigma(\cdot)]X^\Sigma$ with the elastically reflected one is measure-preserving.

Finally, use of the Poincaré recurrence theorem (9) gives (iv) as a consequence of (iii) and of the measurability of τ^Σ.

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REFERENCES

1. D. Ruelle, *Statistical Mechanics: Rigorous Results*, W. A. Benjamin (1969).
2. E. H. Kennard, *Kinetic Theory of Gases*, McGraw-Hill, New York and London (1938); R. H. Fowler, *Statistical Mechanics*, Cambridge at the University Press (1936).
3. J. L. Lebowitz, Modified virial theorem for total momentum fluctuations, *Phys. Rev.* **109**:1464 (1958).
4. C. Marchioro, A. Pellegrinotti, E. Presutti, and M. Pulvirenti, On the dynamics of particles moving in a bounded region: a measure theoretical approach, Nota Interna Ist. Mat. Univ. Roma, Italy.
5. G. Gallavotti and S. Miracle-Sole, Absence of phase transitions in hard-core one-dimensional systems with long-range interactions, *J. Math. Phys.* **11**:147 (1970) [due to a typographical error, the title page of this paper bears the date 1969].
6. N. Dunford and J. T. Schwartz, *Linear Operators*. Part I, Interscience, New York (1958).
7. E. A. Milne, An extension of the theorem of the virial, *Phil. Mag.* **50**:409 (1925).
8. W. Ambrose, Representation of ergodic flows, *Ann. of Math.* **42**:723 (1942); W. Ambrose and S. Kakutani, Structure and continuity of measurable flows, *Duke Math. J.* **9**:25 (1942).
9. P. R. Halmos, *Lectures on Ergodic Theory*, Publ. Math. Soc. Japan; Math. Soc. Japan, Tokyo (1956); reprint Chelsea, New York (1960).