On the Partition Function of a One-Dimensional Gas*

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A method is presented for calculating the grand-partition function of a one-dimensional gas with the potential $V(x) = +\infty$ for $0 \leq x < \delta$ and $V(x) = -\alpha\, e^{-\gamma x}$ for $x \geq \delta$.

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THE paucity of exact calculations of partition functions makes it desirable to search for cases in which such calculations can be performed.

In this note we shall show how to calculate the grand-partition function of a one-dimensional gas with the potential $V(x)$ given by the formula

$$V(x) = \begin{cases} +\infty, & 0 \leq x < \delta, \\ -\alpha \exp(-\gamma x), & x \geq \delta. \end{cases} \tag{1.1}$$

The crucial feature of the potential responsible for the success of the calculation is that $\exp(-\gamma\,|t|)$ is the correlation function of a *stationary, Gaussian, Markoffian* process (the Ornstein-Uhlenbeck process).

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Let

$$\frac{Q_n}{n!} = \frac{1}{n!}\int_0^L \cdots \int_0^L \exp\left\{-\frac{1}{kT} \cdot \sum_{1\leq i<j\leq n} V(|t_j - t_i|)\right\} dt_1 \cdots dt_n \tag{2.1}$$

and set

$$\psi(x) = \begin{cases} 1, & |x| < \delta, \\ 0, & |x| > \delta. \end{cases} \tag{2.2}$$

We can write now

$$\frac{Q_n}{n!} = \frac{1}{n!}\int_0^L \cdots \int_0^L \exp\left\{\frac{\alpha}{kT} \sum_{1\leq i<j\leq n} e^{-\gamma|t_j - t_i|}\right\} \cdot \prod_{1\leq i<j\leq n} [1 - \psi(|t_j - t_i|)]\, dt_1 \cdots dt_n$$

or, setting

$$\alpha/kT = \beta, \tag{2.3}$$

$$\frac{Q_n}{n!} = \exp\left(-\frac{n\beta}{2}\right)\int_0^L \cdots \int_0^L \exp\left\{\frac{\beta}{2} \sum_{i,j=1}^{n} e^{-\gamma|t_j - t_i|}\right\} \cdot \prod_{1\leq i<j\leq n} [1 - \psi(|t_j - t_i|)]\, dt_1 \cdots dt_n. \tag{2.4}$$

Since the integrand in (2.4) is symmetric in the variables $t_1, \cdots, t_n$ we have

$$\frac{Q_n}{n!} = \exp\left(-\frac{n\beta}{2}\right) \cdot \int \cdots \int_{0<t_1<t_2<\cdots<t_n<L} \exp\left\{\frac{\beta}{2} \sum_{i,j=1}^{n} e^{-\gamma|t_j - t_i|}\right\} \cdot \prod_{1\leq i<j\leq n} [1 - \psi(|t_j - t_i|)]\, dt_1 \cdots dt_n. \tag{2.5}$$

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Now, for $0 < t_1 < \cdots < t_n$ we have

$$\prod_{1\leq i<j\leq n} [1 - \psi(|t_j - t_i|)] = \prod_{j=1}^{n-1} [1 - \psi(t_{j+1} - t_j)], \tag{3.1}$$

and

$$\exp\left\{\frac{\beta}{2} \sum_{i,j=1}^{n} e^{-\gamma|t_j - t_i|}\right\} = E(\exp\{\beta^{\frac{1}{2}}[X(t_1) + \cdots + X(t_n)]\}), \tag{3.2}$$

where $X(t)$ is a stationary Gaussian process whose covariance is

$$E\{X(t)X(t+\tau)\} = \exp(-\gamma\,|\tau|). \tag{3.3}$$

It is well known that a stationary Gaussian process with covariance (3.3) is Markoffian, i.e.,

$$E(\exp\{\beta^{\frac{1}{2}}[X(t_1) + \cdots + X(t_n)]\}) = \int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} \exp\{\beta^{\frac{1}{2}}(x_1 + \cdots + x_n)\} \cdot W(x_1)P(x_1 \mid x_2; t_2 - t_1) \cdots P(x_{n-1} \mid x_n; t_n - t_{n-1})\, dx_1 \cdots dx_n, \tag{3.4}$$

where

$$W(x) = \frac{1}{(2\pi)^{\frac{1}{2}}} \exp\left(-\frac{x^2}{2}\right) \tag{3.5}$$

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and

$$P(x \mid y; t) = \frac{\exp\left\{-\frac{(y - xe^{-\gamma t})^2}{2(1 - e^{-2\gamma t})}\right\}}{[2\pi(1 - e^{-2\gamma t})]^{\frac{1}{2}}}. \quad (3.6)$$

Finally,

$$\frac{Q_n}{n!} = \exp\left(-\frac{n\beta}{2}\right) \cdot \int_{-\infty}^{\infty} \cdots \int \exp\{\beta^{\frac{1}{2}}(x_1 + \cdots + x_n)\} W(x_1) \cdot \int_{0<t_1<\cdots<t_n<L} \cdots \int \prod_{j=1}^{n-1} P(x_j \mid x_{j+1}; t_{j+1} - t_j) \cdot (1 - \psi(t_{j+1} - t_j)\, dt_1 \cdots dt_n.\, dx_1 \cdots dx_n. \quad (3.7)$$

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Upon introducing Laplace transforms we get

$$\int_0^{\infty} \exp(-sL) \frac{Q_n(L)}{n!}\, dL = \frac{1}{s^2} \exp\left(-\frac{n\beta}{2}\right) \cdot \int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} \exp\{\beta^{\frac{1}{2}}(x_1 + \cdots + x_n)\} \cdot W(x_1) \prod_{j=1}^{n-1} p_s(x_j \mid x_{j+1})\, dx_1 \cdots dx_n, \quad (4.1)$$

$$p_s(x \mid y) = \int_0^{\infty} \exp(-st) P(x \mid y; t)[1 - \psi(t)]\, dt = \int_{\delta}^{\infty} \exp(-st) P(x \mid y; t)\, dt. \quad (4.2)$$

Now let

$$G(L; z) = \sum_{n=1}^{\infty} \frac{z^n Q_n(L)}{n!} \quad (4.3)$$

be the grand-partition function.

We have

$$\int_0^{\infty} \exp(-sL) G(L; z)\, dL = \frac{1}{s^2} \sum_{n=1}^{\infty} \left[z \exp\left(-\frac{\beta}{2}\right)\right]^n \cdot \int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} \exp\{\beta^{\frac{1}{2}}(x_1 + \cdots + x_n)\} \cdot W(x_1) \prod_{j=1}^{n-1} p_s(x_j \mid x_{j+1})\, dx_1 \cdots dx_n, \quad (4.4)$$

and it is convenient to introduce the *symmetric* kernel

$$K_s(x, y) = \exp\left(\frac{x\beta^{\frac{1}{2}}}{2}\right) \frac{W(x) p_s(x \mid y)}{[W(x)W(y)]^{\frac{1}{2}}} \exp\left(\frac{y\beta^{\frac{1}{2}}}{2}\right). \quad (4.5)$$

In the next section we prove that this kernel is of the Hilbert-Schmidt type and that consequently it has eigenvalue and eigenfunctions.

In terms of this kernel the multiple integral in (4.4) can be written as

$$\int_{-\infty}^{\infty} \cdots \int [W(x_1)]^{\frac{1}{2}} \cdot \exp\left(\frac{x_1\beta^{\frac{1}{2}}}{2}\right) K_s(x_1, x_2) K_s(x_2, x_3) \cdots K_s(x_{n-1}, x_n) \cdot [W(x_n)]^{\frac{1}{2}} \exp\left(\frac{x_n\beta^{\frac{1}{2}}}{2}\right) dx_1 \cdots dx_n = \sum_{j=1}^{\infty} \lambda_j^{n-1}(s) \left[\int_{-\infty}^{\infty} [W(x)]^{\frac{1}{2}} \psi_j(x) \cdot \exp\left(\frac{x\beta^{\frac{1}{2}}}{2}\right) dx\right]^2, \quad (4.6)$$

where the ψ_j's and λ_j's are the eigenvalues and normalized eigenfunctions of the integral equation

$$\int_{-\infty}^{\infty} K_s(x, y) \psi(y)\, dy = \lambda \psi(x). \quad (4.7)$$

It goes without saying that the ψ's (like the λ's) depend on s.

It may be pointed out that it is well known that

$$W(x) P(x \mid y; t) = \sum_{k=0}^{\infty} \frac{\exp(-x^2/2) H_k(x) \exp(-y^2/2) H_k(y)}{2\pi k!} \cdot \exp(-k\gamma t),$$

where H_k is the kth Hermite polynomial.

It thus follows that

$$K_s(x, y) = \exp\left[\frac{\beta^{\frac{1}{2}}(x + y)}{2}\right] \cdot \sum_{k=0}^{\infty} \frac{\exp(-x^2/4) H_k(x) \exp(-y^2/4) H_k(y)}{(2\pi)^{\frac{1}{2}} k!} \cdot \int_{\delta}^{\infty} \exp(-st) \exp(-k\gamma t)\, dt, \quad (4.8)$$

and it follows, in particular, that K_s is positive-definite.

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We now prove that $K_s(x, y)$ is a Hilbert-Schmidt kernel provided $\delta > 0$. We must prove that

$$\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} K_s^2(x, y)\, dx\, dy < \infty. \quad (5.1)$$

We have

$$K_s^2(x, y) = K_s(x_1 y)K_s(y, x)$$
$$= \exp\{\beta^{\frac{1}{2}}(x + y)\}p_s(x \mid y)p_s(y \mid x)$$
$$= \exp\{\beta^{\frac{1}{2}}(x + y)\} \int_s^\infty \int_s^\infty P(x \mid y; t_1)P(y \mid x; t_2) \cdot \exp\{-s(t_1 + t_2)\}\, dt_1\, dt_2,$$

and consequently

$$\int_{-\infty}^\infty \int_{-\infty}^\infty K_s^2(x, y)\, dx\, dy = \int_s^\infty \int_s^\infty \exp\{-s(t_1 + t_2)\}\, dt_1\, dt_2 \cdot \int_{-\infty}^\infty \int P(x \mid y; t_1)P(y \mid x; t_2) \cdot \exp\{\beta^{\frac{1}{2}}(x + y)\}\, dx\, dy.$$

Now

$$\int_{-\infty}^\infty \int_{-\infty}^\infty P(x \mid y; t_1)P(y \mid x; t_2) \exp\{\beta^{\frac{1}{2}}(x + y)\}\, dx\, dy = \int_{-\infty}^\infty \int \frac{W(x)P(x \mid y; t_1)}{[W(x)W(y)]^{\frac{1}{2}}} \frac{W(y)P(y \mid x; t_2)}{[W(x)W(y)]^{\frac{1}{2}}} \cdot \exp\{\beta^{\frac{1}{2}}(x + y)\}\, dx\, dy,$$

and hence by Schwarz's inequality

$$\int_{-\infty}^\infty \int_{-\infty}^\infty P(x \mid y; t_1)P(y \mid x; t_2) \exp\{\beta^{\frac{1}{2}}(x + y)\}\, dx\, dy$$
$$\leq \left(\int_{-\infty}^\infty \int_{-\infty}^\infty \frac{W(x)}{W(y)} P^2(x \mid y; t_1) \exp\{\beta^{\frac{1}{2}}(x + y)\}\, dx\, dy\right)^{\frac{1}{2}}$$
$$\cdot \left(\int_{-\infty}^\infty \int_{-\infty}^\infty \frac{W(y)}{W(x)} P^2(x \mid y; t_2) \exp\{\beta^{\frac{1}{2}}(x + y)\}\, dx\, dy\right)^{\frac{1}{2}}.$$

An elementary calculation yields

$$\int_{-\infty}^\infty \int_{-\infty}^\infty \frac{W(y)}{W(x)} P^2(x \mid y; t)\, dx\, dy = \frac{\exp\left\{\beta\left(\frac{1 + e^{-\gamma t}}{1 - e^{-\gamma t}}\right)\right\}}{2\pi(1 - e^{-2\gamma t})},$$

and (5.1) follows almost immediately.

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Let $\lambda_1(s)$ be the largest eigenvalue. Then for

$$0 < z < \frac{\exp(\beta/2)}{\lambda_1(s)}, \tag{6.1}$$

it follows [by substituting (4.6) into (4.4)] that

$$\int_0^\infty \exp(-sL)G(L; z)\, dL = \frac{1}{s^2} z \exp(-\beta/2) \cdot \sum_{j=1}^\infty \frac{\left\{\int_{-\infty}^\infty \exp\left(\frac{\beta x}{2}\right)[W(x)]^{\frac{1}{2}}\psi_j(x)\, dx\right\}^2}{1 - \lambda_j z \exp(-\beta/2)}, \tag{6.2}$$

and in particular the Laplace integral on the left-hand side of (6.2) converges.

On the other hand, it follows easily that, if

$$z = \frac{\exp(\beta/2)}{\lambda_1(s)}, \tag{6.3}$$

the Laplace integral diverges.

In the next section we prove that $\lambda_1(s)$ is a decreasing function of s and

$$\lim_{s\to 0} \lambda_1(s) = \infty, \qquad \lim_{s\to\infty} \lambda_1(s) = 0. \tag{6.4}$$

It follows from this that (6.3) has a solution for every $z > 0$ and, moreover, that the solution is the *abscissa of convergence* of the Laplace transform.

On the other hand, Yang and Lee[1] have shown that

$$\lim_{L\to\infty} \frac{1}{L} \log G(L; z) = \chi(z) \tag{6.5}$$

exists and consequently $\chi(z)$ is clearly the abscissa of convergence. Thus

$$\lambda_1[\chi(z)] = \frac{\exp(\beta/2)}{z}, \tag{6.6}$$

which, in principle, determines $\chi(z)$ and hence the equation of state. As is well known,

$$p/kT = \chi(z), \tag{6.7}$$

$$\rho = z\chi'(z), \tag{6.8}$$

where p is the pressure and ρ the density.

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We now prove the properties of $\lambda_1(s)$ which have been used in Sec. 6.

Recall that

$$K_s(x, y) = \exp\left\{\frac{\beta^{\frac{1}{2}}}{2}(x + y)\right\}\left(\frac{W(x)}{W(y)}\right)^{\frac{1}{2}} \cdot \int_s^\infty \exp(-st)P(x \mid y; t)\, dt$$

can be written in the form (4.8) whence it follows that if $s_1 > s_2$ and $\varphi \in L^2(-\infty, \infty)$, then

[1] C. N. Yang and T. D. Lee, Phys. Rev. 57, 404 (1952).

$$\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} K_{s_1}(x, y)\varphi(x)\varphi(y)\,dx\,dy \leq \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} K_{s_2}(x, y)\varphi(x)\varphi(y)\,dx\,dy.$$

Hence by the Weyl-Courant lemma

$$\lambda_j(s_1) \leq \lambda_j(s_2) \tag{7.1}$$

for $j = 1, 2, \cdots$.

Next from considerations of Sec. 5 it follows that

$$\lim_{s\to\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} K_s^2(x, y)\,dx\,dy = 0,$$

and consequently

$$\lim_{s\to\infty}\lambda_1(s) = 0. \tag{7.2}$$

There remains to prove that

$$\lim_{s\to 0}\lambda_1(s) = \infty. \tag{7.3}$$

We do this by noting that

$$\lambda_1(s) \geq \frac{\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\varphi(x)K_s(x, y)\varphi(y)\,dx\,dy}{\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\varphi^2(x)\,dx\,dy}$$

and taking

$$\varphi(x) = \exp\left(\frac{x\beta^{\frac{1}{2}}}{2}\right)[W(x)]^{\frac{1}{2}}.$$

An easy calculation yields

$$\lambda_1(s) \geq \exp(\beta/2) \cdot\int_{\delta}^{\infty}\exp(-st)\exp\{\beta\exp(-\gamma t)\}\,dt; \tag{7.4}$$

hence (7.3) follows at once.

It should be pointed out that

$$\exp(\beta/2)\int_{\delta}^{\infty}\exp(-st)\exp\{\beta\exp(-\gamma t)\}\,dt$$

corresponds to the "nearest-neighbor" approximation. An extension to an arbitrary (but *finite*) number of neighbors was given by van Hove.[2]

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Certain general conclusions can be drawn from the preceding discussion.

(a) The gas does not condense. This follows from the fact that $\lambda_1(s)$ is a monotonic function of s which varies from 0 to ∞ [see (7.1), (7.2), and (7.3)] combined with the fact that the Fredholm determinant of our integral equation is an analytic function of s for $\operatorname{Re} s > 0$.

[2] L. van Hove, Physica 16, 137 (1950).

(b) The equation of state in the p, ρ variables is easily seen to be

$$-\frac{\lambda_1'(p/kT)}{\lambda_1(p/kT)} = \frac{1}{\rho},$$

but the "explicitness" of this formula is illusory since λ_1 is not really known as a function of s.

(c) From (4.8) one sees that for small s

$$K_s(x, y) \sim \frac{\exp(-s\delta)}{s} \cdot\exp[\beta^{\frac{1}{2}}(x + y)]\frac{\exp\left(-\frac{x^2 + y^2}{4}\right)}{(2\pi)^{\frac{1}{2}}},$$

and one can use this to calculate $\lambda_1(s)$ by a perturbation calculation.

In principle this would allow one to determine the expansion

$$\lambda_1(s) = \frac{\alpha_{-1}}{s} + \alpha_0 + \alpha_1 s + \alpha_2 s^2 + \cdots.$$

By the basic relation

$$\lambda_1[\chi(z)] = \frac{\exp(\beta/2)}{z},$$

one sees that the α's are related in a complicated way to the familiar b_l's.

It thus follows that an attempt to determine the equation of state by calculating the b_l's is in effect equivalent to finding $\lambda_1(s)$ by a perturbation technique.

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It may be worthy of mention that a slight modification of the method described in the foregoing permits one to calculate the partition function for a one-dimensional Ising model in which the interaction decreases exponentially.

Let

$$Q_n = \sum\exp\left\{\frac{J}{kT}\sum_{1\leq i<j\leq n}\exp(-\gamma\mid j - i\mid)\mu_i\mu_j\right\}, \tag{9.1}$$

where the outer summation is over $\mu_1, \cdots, \mu_n$, each μ assuming values $+1$ and -1.

By setting

$$\beta = J/kT \tag{9.2}$$

and noting that

$$\sum_{1\leq i<j\leq n}\exp(-\gamma\mid j - i\mid)\mu_i\mu_j = \frac{1}{2}\sum_{i,j=1}^{n}\exp(-\gamma\mid j - i\mid)\mu_i\mu_j - \frac{n}{2}, \tag{9.3}$$

we can write

$$Q_n = \exp\left(-\frac{n\beta}{2}\right)$$

$$\cdot \sum \exp\left\{\frac{\beta}{2}\sum_{i,j=1}^{n} \exp(-\gamma\mid j-i\mid)\mu_i\mu_j\right\}. \quad (9.4)$$

Now

$$\exp\left\{\frac{\beta}{2}\sum_{i,j=1}^{n} \exp(-\gamma\mid j-i\mid)\mu_i\mu_j\right\}$$

$$= E\left\{\exp\left[\beta^{\frac{1}{2}}\sum_{i=1}^{n} X(i)\mu_i\right]\right\}, \quad (9.5)$$

where $X(t)$ is the process defined in Sec. 3.

Thus

$$Q_n = 2^n \exp\left(-\frac{n\beta}{2}\right)E\left\{\prod_{i=1}^{n}\cosh \beta^{\frac{1}{2}}X(i)\right\}$$

$$= 2^n \exp\left(-\frac{n\beta}{2}\right)$$

$$\cdot \int_{-\infty}^{\infty}\cdots\int_{-\infty}^{\infty}\cosh(\beta^{\frac{1}{2}}x_1)\cdots\cosh(\beta^{\frac{1}{2}}x_n) \quad (9.6)$$

$$\cdot W(x_1)P(x_1\mid x_2;1)\cdots$$

$$P(x_{n-1}\mid x_n;1)\,dx_1\cdots dx_n.$$

It now follows (as in Sec. 4) that

$$\lim_{n\to\infty}(Q_n)^{1/n} = 2\exp(-\beta/2)\lambda_1, \quad (9.7)$$

where λ_1 is the *largest* eigenvalue of the integral equation

$$\int_{-\infty}^{\infty}[\cosh(\beta^{\frac{1}{2}}x)]^{\frac{1}{2}}\frac{W(x)P(x\mid y;1)}{[W(x)W(y)]^{2}}$$

$$\cdot[\cosh(\beta^{\frac{1}{2}}y)]^{\frac{1}{2}}\varphi(y)\,dy = \lambda\varphi(x). \quad (9.8)$$

Although this integral equation cannot be solved explicitly it follows easily that the model will not exhibit a phase transition.

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Contribution to the Theory of Brownian Motion*

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The classical theory of Brownian motion of a periodic system is generalized to include the case where the period of the system is very short compared with times characteristic of its interaction with the environment. The system is described in terms of action and phase variables, which are constants of the motion in the absence of interactions. The probability density of the system, averaged over a time which is very long compared with a period of the motion, and long enough to include many interactions, is shown to be a solution of a Fokker-Planck equation in action-phase variables. Conditions for this are that the interaction is sufficiently weak and that the environment remains in thermal equilibrium. Explicit expressions for the friction coefficients are obtained. When the probability density of the system is independent of its phase, its irreversible behavior can be described as a random walk in action space. This is a reasonable classical analog to the quantum-statistical description by means of the Pauli equation. The properties of a harmonic oscillator with a special interaction are considered in detail; it is shown that the friction coefficients are proportional to the spectral density of a fluctuating force associated with the interaction, evaluated at the frequency of the oscillator.

INTRODUCTION

THIS work arose from curiosity about whether or not there is a simple connection between two different and widely used points of view in the theory of relaxation processes. Some phenomena (e.g., dielectric relaxation) have been treated in the framework of the classical theory of Brownian motion, and others (e.g., vibrational relaxation) have been discussed using the Pauli equation of quantum statistical mechanics. These two approaches appear to have different ranges of application and validity, but there ought to be some underlying similarities.

Another, more practical reason than just curiosity for looking for a connection between these approaches is that it is often convenient and

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