G25.2651: Statistical Mechanics

Notes for Lecture 13

I. THE FUNCTIONAL INTEGRAL REPRESENTATION OF THE PATH INTEGRAL

A. The continuous limit

In taking the limit $P \to \infty$, it will prove useful to define a parameter

$$\varepsilon = \frac{\beta\hbar}{P}$$

so that $P \to \infty$ implies $\varepsilon \to 0$. In terms of ε, the partition function becomes

$$Q(\beta) = \lim_{P\to\infty,\varepsilon\to 0} \left(\frac{m}{2\pi\varepsilon\hbar}\right)^{P/2} \int dx_1 \cdots dx_P \exp\left[-\frac{\varepsilon}{\hbar}\sum_{i=1}^{P}\left(\frac{m}{2}\left(\frac{x_{i+1}-x_i}{\varepsilon}\right)^2 + U(x_i)\right)\right]\Bigg|_{x_{P+1}=x_1}$$

We can think of the points $x_1, ..., x_P$ as specific points of a continuous functions $x(\tau)$, where

$$x_k = x(\tau = (k-1)\varepsilon)$$

such that $x(0) = x(\tau = P\varepsilon) = x(\tau = \beta\hbar)$:

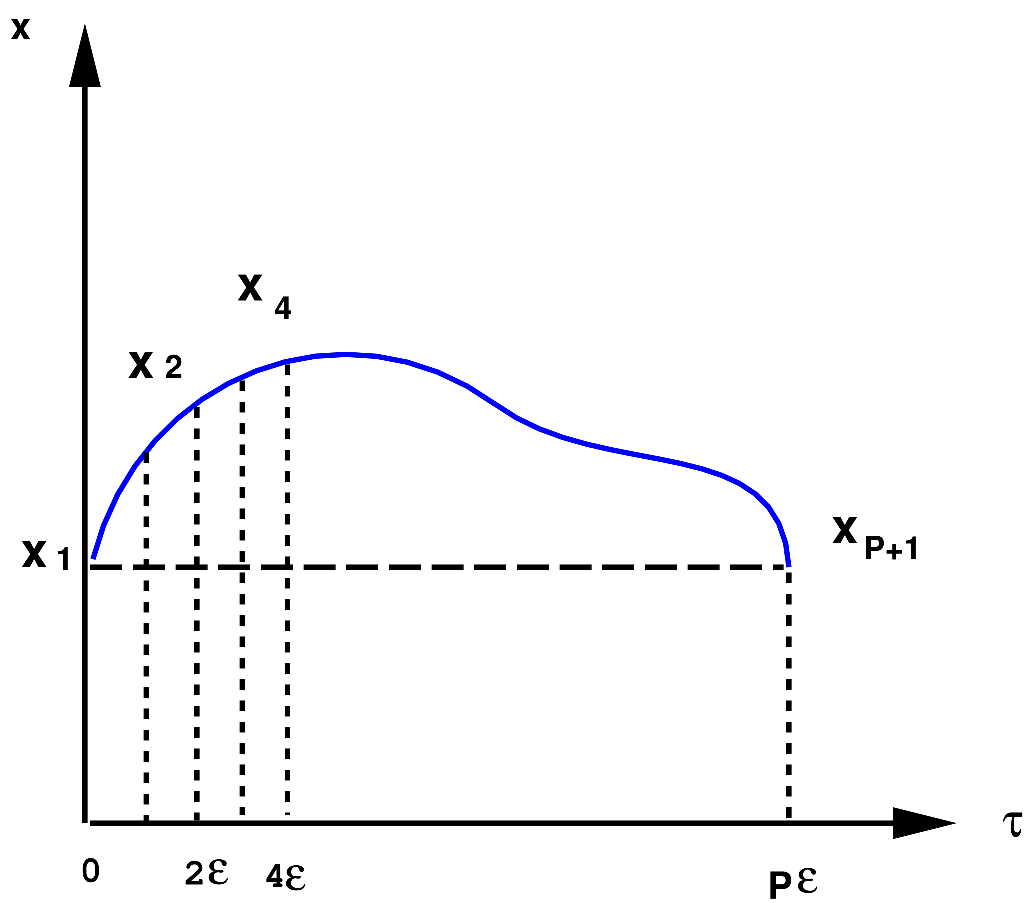

FIG. 1.

Note that

$$\lim_{\varepsilon\to 0}\left(\frac{x_{k+1}-x_k}{\varepsilon}\right) = \lim_{\varepsilon\to 0}\left(\frac{x(k\varepsilon)-x((k-1)\varepsilon)}{\varepsilon}\right) = \frac{dx}{d\tau}$$

and that the limit

$$\lim_{P\to\infty,\varepsilon\to 0}\frac{\varepsilon}{\hbar}\sum_{i=1}^{P}\left[\frac{m}{2}\left(\frac{x_{i+1}-x_i}{\varepsilon}\right)^2 + U(x_i)\right]$$

is just a Riemann sum representation of the continuous integral

$$\frac{1}{\hbar}|\int_0^{\beta\hbar} d\tau\left[\frac{m}{2}\left(\frac{dx}{d\tau}\right)^2 + U(x(\tau))\right]$$

Finally, the measure

$$\lim_{P\to\infty,\varepsilon\to 0}\left(\frac{m}{2\pi\varepsilon\hbar^2}\right)^{P/2} dx_1\cdots dx_P$$

represents an integral overa all values that the function $x(\tau)$ can take on between $\tau = 0$ and $\tau = \beta\hbar$ such that $x(0) = x(\beta\hbar)$. We write this symbolically as $\mathcal{D}x(\cdot)$. Therefore, the $P\to\infty$ limit of the partition function can be written as

$$\begin{aligned} Q(\beta) &= \int dx \int_{x(0)=x}^{x(\beta\hbar)=x}\mathcal{D}x(\cdot)\exp\left[-\frac{1}{\hbar}\int_0^{\beta\hbar} d\tau\left(\frac{m}{2}\dot{x}^2 + U(x(\tau))\right)\right] \\ &= \oint \mathcal{D}x(\cdot)\exp\left[-\frac{1}{\hbar}\int_0^{\beta\hbar} d\tau\left(\frac{m}{2}\dot{x}^2 + U(x(\tau))\right)\right] \end{aligned}$$

The above expression in known as a *functional integral.* It says that we must integrate over all functions (i.e., all values that an arbitrary function $x(\tau)$ may take on) between the values $\tau = 0$ and $\tau = \beta\hbar$. It must really be viewed as the limit of the discretized integral introduced in the last lecture. The integral is also referred to as a *path integral* because it implies an integration over all paths that a particle might take between $\tau = 0$ and $\tau = \beta\hbar$ such that $x(0) = x(\beta\hbar$, where the paths are paramterized by the variable τ (which is not time!). The second line in the above expression, which is equivalent to the first, indicates that the integration is taken over all paths that begin and end at the same point, plus a final integration over that point.

The above expression makes it clear how to represent a general density matrix element $\langle x|\exp(-\beta H)|x'\rangle$:

$$\langle x|e^{-\beta H}|x'\rangle = \int_{x(0)=x}^{x(\beta\hbar)=x'}\mathcal{D}x(\cdot)\exp\left[-\frac{1}{\hbar}\int_0^{\beta\hbar} d\tau\left(\frac{m}{2}\dot{x}^2 + U(x(\tau))\right)\right]$$

which indicates that we must integrate over all functions $x(\tau)$ that begin at x at $\tau = 0$ and end at x' at $\tau = \beta\hbar$:

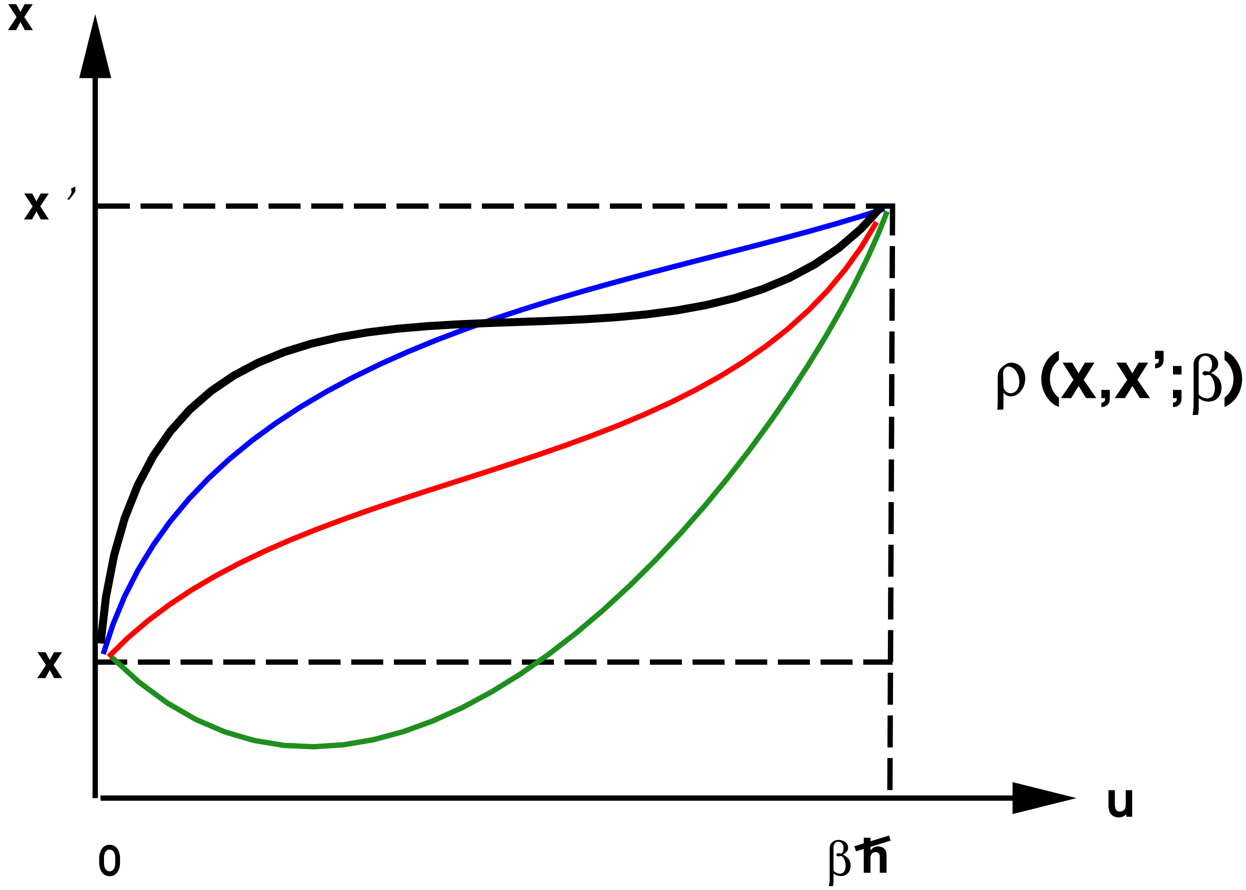

FIG. 2.

Similarly, diagonal elements of the density matrix, used to compute the partition function, are calculated by integrating over all periodic paths that satisfy $x(0) = x(\beta\hbar) = x$:

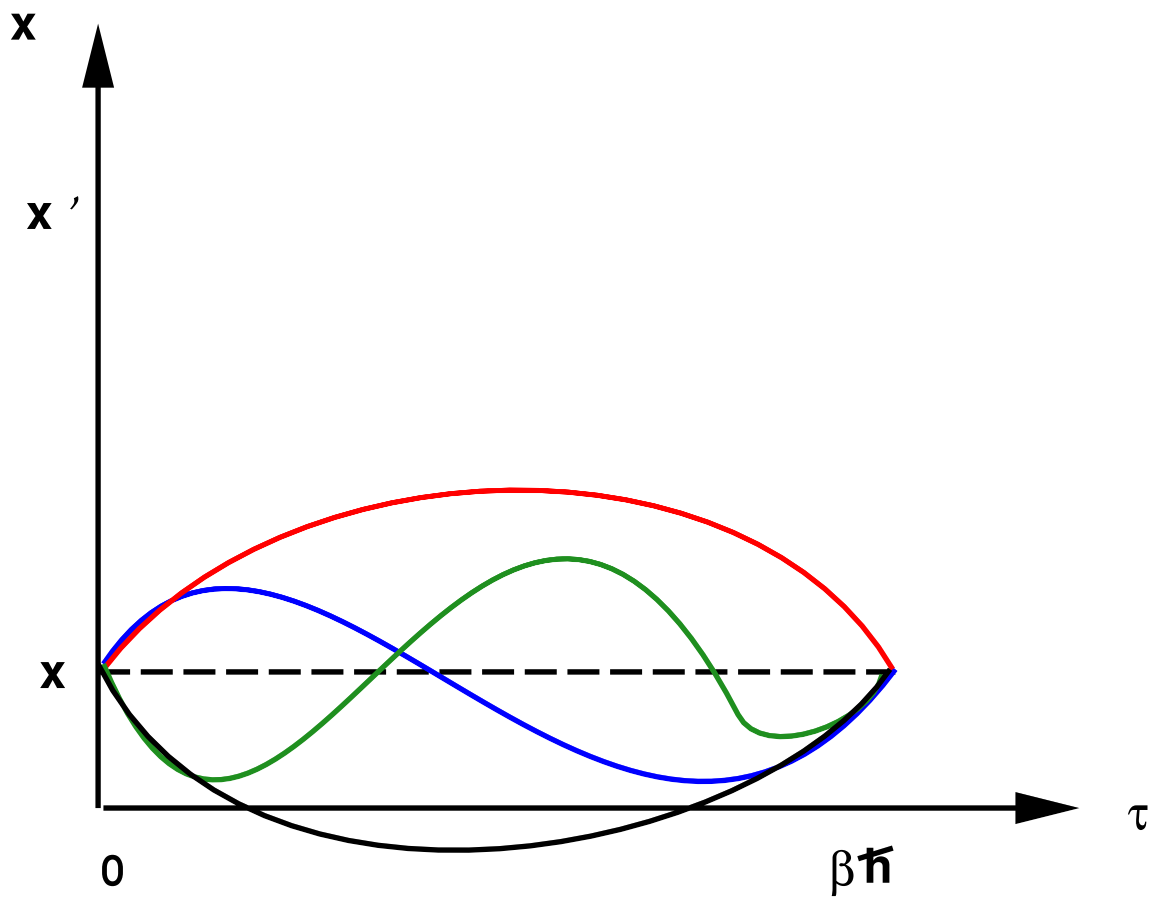

FIG. 3.

Note that if we let $\beta = it/\hbar$, then the density matrix becomes

$$\rho(x, x'; it/\hbar) = \langle x|e^{-iHt/\hbar}|x'\rangle = U(x, x'; t)$$

which are the coordinate space matrix elements of the quantum time evolution operator. If we make a change of variables $\tau = is$ in the path integral expression for the density matrix, we find that the quantum propagator can also be expressed as a path integral:

$$U(x, x'; t) = \langle x|e^{-iHt/\hbar}|x'\rangle = \int_{x(0)=x}^{x(t)=x'} \mathcal{D}x(\cdot) \exp\left[\frac{i}{\hbar}\int_0^t ds\left(\frac{m}{2}\dot{x}(s) - U(x(s))\right)\right]$$

Such a variable transformation is known as a *Wick rotation*. This nomenclature comes about by viewing time as a complex quantity. The propagator involves real time, while the density matrix involves a transformation $t = -i\beta\hbar$ to the imaginary time axis. It is because of this that the density matrix is sometimes referred to as an *imaginary time path integral*.

B. Dominant paths in the propagator and density matrix

Let us first consider the real time quantum propagator. The quantity appearing in the exponential is an integral of

$$\frac{1}{2}m\dot{x}^2 - U(x) \equiv L(x, \dot{x})$$

which is known as the Lagrangian in classical mechanics. We can ask, which paths will contribute most to the integral

$$\int_0^t ds\left[\frac{m}{2}\dot{x}^2(s) - U(x(s))\right] = \int_0^t dsL(x(s), \dot{x}(s)) = S[x]$$

known as the *action integral.* Since we are integrating over a complex exponential $\exp(iS/\hbar)$, which is oscillatory, those paths away from which small deviations cause no change in S (at least to first order) will give rise to the dominant contribution. Other paths that cause $\exp(iS/\hbar)$ to oscillate rapidly as we change from one path to another will give rise to phase decoherence and will ultimately cancel when integrated over. Thus, we consider two paths $x(s)$ and a nearby one constructed from it $x(s) + \delta x(s)$ and demand that the change in S between these paths be 0

$$S[x + \delta x] - S[x] = 0$$

Note that, since $x(0) = x$ and $x(t) = x'$, $\delta x(0) = \delta x(t) = 0$, since *all* paths must begin at x and end at x'. The change in S is

$$\delta S = S[x + \delta x] - S[x] = \int_0^t ds L(x + \delta x, \dot{x} + \delta \dot{x}) - \int_0^t ds L(x, \dot{x})$$

Expanding the first term to first order in δx, we obtain

$$\delta S = \int_0^t ds \left[L(x, \dot{x}) + \frac{\partial L}{\partial \dot{x}} \delta \dot{x} + \frac{\partial L}{\partial x} \delta x \right] - \int_0^t L(x, \dot{x}) = \int_0^t ds \left[\frac{\partial L}{\partial \dot{x}} \delta \dot{x} + \frac{\partial L}{\partial x} \delta x \right]$$

The term proportional to $\delta \dot{x}$ can be handled by an integration by parts:

$$\int_0^t ds \frac{\partial L}{\partial \dot{x}} \delta \dot{x} = \int_0^t ds \frac{\partial L}{\partial \dot{x}} \frac{d}{dt} \delta x = \left. \frac{\partial L}{\partial \dot{x}} \delta x \right|_0^t - \int_0^t ds \frac{d}{dt} \frac{\partial L}{\partial \dot{x}} \delta x$$

because δx vanishes at 0 and t, the surface term is 0, leaving us with

$$\delta S = \int_0^t ds \left[-\frac{d}{dt} \frac{\partial L}{\partial \dot{x}} + \frac{\partial L}{\partial x} \right] \delta x = 0$$

Since the variation itself is arbitrary, the only way the integral can vanish, in general, is if the term in brackets vanishes:

$$\frac{d}{dt} \frac{\partial L}{\partial \dot{x}} - \frac{\partial L}{\partial x} = 0$$

This is known as the Euler-Lagrange equation in classical mechanics. For the case that $L = m\dot{x}/2 - U(x)$, they give

$$\frac{d}{dt}(m\dot{x}) + \frac{\partial U}{\partial x} = 0$$

$$m\ddot{x} = -\frac{\partial U}{\partial x}$$

which is just Newton's equation of motion, subject to the conditions that $x(0) = x$, $x(t) = x'$. Thus, the classical path and those near it contribute the most to the path integral.

The classical path condition was derived by requiring that $\delta S = 0$ to first order. This is known as an action *stationarity* principle. However, it turns out that there is also a principle of *least action*, which states that the classical path minimizes the action as well. This is an important consideration when deriving the dominant paths for the density matrix, which takes the form

$$\rho(x, x'; \beta) = \int_{x(0)=x}^{x(\beta\hbar=x'} \mathcal{D}x(\cdot) \exp \left[-\frac{1}{\hbar} \int_0^{\beta\hbar} d\tau \left(\frac{m}{2} \dot{x}(\tau) + U(x(\tau)) \right) \right]$$

The action appearing in this expression is

$$S_E[x] = \int_0^{\beta\hbar} d\tau \left[\frac{m}{2} \dot{x}^2 + U(x(\tau)) \right] = \int_0^{\beta\hbar} d\tau H(x, \dot{x})$$

which is known as the *Euclidean action* and is just the integral over a path of the total energy or *Euclidean Lagrangian* $H(x, \dot{x})$. Here, we see that a minimum action principle is needed, since the smallest values of S_E will contribute most to the integral. Again, we require that to first order $S_E[x + \delta x] - S_E[x] = 0$. Applying the same logic as before, we obtain the condition

$$\frac{d}{d\tau}\frac{\partial H}{\partial \dot{x}} - \frac{\partial H}{\partial x} = 0$$
$$m\ddot{x} = \frac{\partial}{\partial x}U(x)$$

which is just Newton's equation of motion on the inverted potential surface $-U(x)$, subject to the conditions $x(0) = x$, $x(\beta\hbar) = x'$. For the partition function $Q(\beta)$, the same equation of motion must be solved, but subject to the conditions that $x(0) = x(\beta\hbar)$, i.e., periodic paths.

II. DOING THE PATH INTEGRAL: THE FREE PARTICLE

The density matrix for the free particle

$$H = \frac{P^2}{2m}$$

will be calculated by doing the discrete path integral explicitly and taking the limit $P \to \infty$ at the end.

The density matrix expression is

$$\rho(x, x'; \beta) = \lim_{P\to\infty}\left(\frac{mP}{2\pi\beta\hbar^2}\right)^{P/2}\int dx_2\cdots dx_P \exp\left[-\frac{mP}{2\beta\hbar^2}\sum_{i=1}^{P}(x_{i+1}-x_i)^2\right]\Bigg|_{x_1=x,x_{P+1}=x'}$$

Let us make a change of variables to

$$u_1 = x_1$$
$$u_k = x_k - \tilde{x}_k$$
$$\tilde{x}_k = \frac{(k-1)x_{k+1} + x_1}{k}$$

The inverse of this transformation can be worked out explicitly, giving

$$x_1 = u_1$$
$$x_k = \sum_{l=1}^{P+1}\frac{k-1}{l-1}u_l + \frac{P-k+1}{P}u_1$$

The Jacobian of the transformation is simply

$$J = \det\begin{pmatrix} 1 & -1/2 & 0 & 0 & \cdots & \\ 0 & 1 & -2/3 & 0 & \cdots & \\ 0 & 0 & 1 & -3/4 & \cdots & \\ 0 & 0 & 0 & 1 & \cdots & \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdots \end{pmatrix} = 1$$

Let us see what the effect of this transformation is for the case $P = 3$. For $P = 3$, one must evaluate

$$(x_1 - x_2)^2 + (x_2 - x_3)^2 + (x_3 - x_4)^2 = (x - x_2)^2 + (x_2 - x_3)^2 + (x_3 - x')^2$$

According to the inverse formula,

$$x_1 = u_1$$
$$x_2 = u_2 + \frac{1}{2}u_3 + \frac{1}{3}x' + \frac{2}{3}x$$
$$x_3 = u_3 + \frac{2}{3}x' + \frac{1}{3}x$$

Thus, the sum of squares becomes

$$(x-x_2)^2+(x_2-x_3)^2+(x_3-x')^2 = 2u_2^2+\frac{3}{2}u_3^2+\frac{1}{3}(x-x')^2$$
$$= \frac{2}{2-1}u_2^2+\frac{3}{3-1}u_3^2+\frac{1}{3}(x-x')^2$$

From this simple exmple, the general formula can be deduced:

$$\sum_{i=1}^{P}(x_{i+1}-x_i)^2 = \sum_{k=2}^{P}\frac{k}{k-1}u_k^2+\frac{1}{P}(x-x')^2$$

Thus, substituting this transformation into the integral gives

$$\rho(x,x';\beta) = \left(\frac{m}{2\pi\beta\hbar^2}\right)^{1/2}\prod_{k=2}^{P}\left(\frac{m_kP}{2\pi\beta\hbar^2}\right)^{1/2}\int du_2\cdots du_P \exp\left[-\sum_{k=2}^{P}\frac{m_kP}{2\beta\hbar^2}u_k^2\right]\exp\left[-\frac{m}{2\beta\hbar^2}(x-x')^2\right]$$

where

$$m_k = \frac{k}{k-1}m$$

and the overall prefactor has been written as

$$\left(\frac{mP}{2\pi\beta\hbar^2}\right)^{P/2} = \left(\frac{m}{2\pi\beta\hbar^2}\right)^{1/2}\prod_{k=2}^{P}\left(\frac{m_kP}{2\pi\beta\hbar^2}\right)^{1/2}$$

Now each of the integrals over the u variables can be integrated over independently, yielding the final result

$$\rho(x,x';\beta) = \left(\frac{m}{2\pi\beta\hbar^2}\right)^{1/2}\exp\left[-\frac{m}{2\beta\hbar^2}(x-x')^2\right]$$

In order to make connection with classical statistical mechanics, we note that the prefactor is just $1/\lambda$, where λ

$$\lambda = \left(\frac{2\pi\beta\hbar^2}{m}\right)^{1/2} = \left(\frac{\beta h^2}{2\pi m}\right)^{1/2}$$

is the kinetic prefactor that showed up also in the classical free particle case. In terms of λ, the free particle density matrix can be written as

$$\rho(x,x';\beta) = \frac{1}{\lambda}e^{-\pi(x-x')^2/\lambda^2}$$

Thus, we see that λ represents the spatial width of a free particle at finite temperature, and is called the "thermal de Broglie wavelength."